Stabilisation of high oxidation-state niobium using 'electron-rich' bicyclic-guanidinates

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Abstract

Synthetic procedures to high oxidation-state complexes of niobium incorporating the bicyclic guanidinate 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidinate, [hpp]⁻, are described. The ligand source was either the *N*-trimethylsilylated guanidine or the lithium guanidinate and the reaction proceeded via elimination of trimethylsilylchloride or transmetallation from $NbCl_5$, respectively. A 1:1 ratio of reagents afforded the mono-ligand product, $Nb(hpp)Cl_4$ (**1**) and crystallisation from acetonitrile afforded the solvated species $Nb(hpp)Cl_4(MeCN)$ (**1a**), demonstrating the ability of the metal centre in **1** to bind small substrate molecules. A 2:1 ratio of lithium guanidinate to $NbCl_5$ resulted in formation of the seven-coordinate, bis-ligand compound, $Nb(hpp)_2Cl_3$ (**2**). These products represent the first examples of guanidinate compounds in which niobium is stable in the +5 oxidation-state, believed to result from enhanced electron donation caused by the bicyclic framework of the ligand. The molecular structures of **1**, **1a** and **2** are reported, presenting for the first time an opportunity to describe bonding parameters within compounds of this type.
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*Keywords:* Niobium; Guanidinate; Crystal structure

1. Introduction

During the last 20 year the amidine and guanidine compounds, RC{NR′}{NHR′} (R = alkyl/aryl and amide, respectively), have been developed as versatile sources of nitrogen based ligands, with examples of coordination to different metals throughout the periodic table [1]. For the case of guanidine-based ligands, coordination has been observed in the neutral, monoanionic and dianionic form, subject to the number of substituents and 'protonation level' of the compound (e.g., tri-

alkyl guanidines may be doubly deprotonated to afford dianions whilst it is not possible to form the corresponding species for the tetra-alkyl guanidines). Amongst the salient features which contribute to the widespread application of these ligands is the capacity to regulate both the steric and electronic environment at a metal centre by designing ligands with different combinations of nitrogen substituents. This is particularly notable in the chemistry of the guanidinate anion where the presence of a zwitterionic resonance (**A**, Scheme 1) will strongly affect the extent of electron-donation to the metal fragment.

In order to maximise the contribution of resonance structure **A** to the overall bonding, work in our laboratory has concentrated on the application of the bicyclic guanidine, 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine, hppH, as a source of ligand (Scheme 2). Constraining the substituents of the tertiary amide in the same

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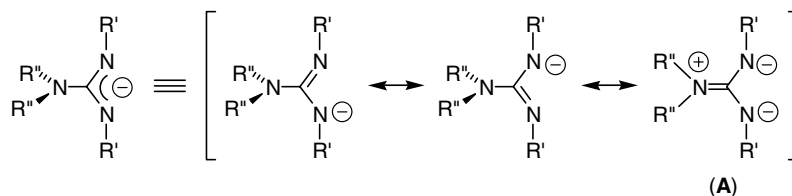
Scheme 1. Resonance structures of the guanidinate anion.
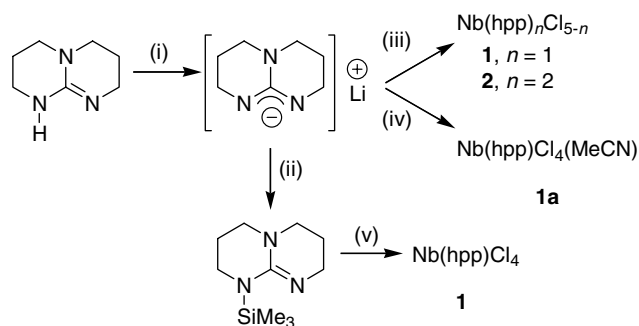
Scheme 2. (i) ^{n}BuLi, THF; (ii) SiMe$_3$Cl, THF; (iii) **1**, NbCl$_5$, toluene or **2**, 0.5 NbCl$_5$, toluene; (iv) NbCl$_5$, MeCN; (v) NbCl$_5$, CH$_2$Cl$_2$.

plane as the 'CN$_2$' amidine component in this molecule ensures a favourable alignment for overlap of the lone-pair with the empty p-orbital of the sp^2-hybridised carbon. Previous work by ourselves and others have shown that the [hpp]$^-$ anion chelates to a range of different main group and transition metals [2], including lithium [3], aluminium [4], tin [5], zinc [6], yttrium [7] and titanium [8,9]. Crystallographic data for a series of mono- and bis-ligand compounds of titanium has indicated notably shorter Ti–N distances in [Ti(hpp)Cl$_2$(μ-Cl)]$_2$ and Ti(hpp)$_2$Cl$_2$ when compared to the corresponding benzamidinate [10] and acyclic guanidinate [11] compounds. These data are commensurate with an increased donation of π-electron density to the d^0-titanium centre, although it is noted that the reduced steric influence of the bicyclic framework may also play a role in the close ligand–metal interactions.

Previous studies by ourselves and others intended to extend the application of guanidinate ligands high oxidation state group 5 metals has, to date, met with limited success. For tantalum, both protonolysis [12] and salt metathesis [13] protocols have been explored as routes to compounds containing monoanionic guanidinates. A number of different product have been isolated in addition to the target molecules, including compounds with the *dianionic* ligand, [(RN=)C(NR)$_2$]$^{2-}$ and those containing the imido group, [NR]$^{2-}$. In an earlier study in our laboratory we sought to utilise [hpp]$^-$ in the stabilisation of high oxidation-state tantalum complexes [14]. However, rather than forming the expected molecular species Ta(hpp)$_n$Cl$_{5-n}$, the ionic species [Ta(hpp)$_4$][TaCl$_6$] was isolated, containing the previously reported eight-coordinate cation, [Ta(hpp)$_4$]$^+$ [15]. A number of high-oxidation state niobium *amidi-*

nate complexes have been reported in the literature [16]; however, this area has not been extended to include guanidinate species. The 2:1 reaction between the lithium salt of the guanidinate anion, [(Me$_3$Si)$_2$NC{NCy}$_2$]$^-$, and NbCl$_5$ resulted in the isolation and characterisation of the reduced Nb(IV) product, Nb[(Me$_3$Si)$_2$NC{NCy}$_2$]$_2$Cl$_2$ In this contribution we wish to report the successful application of the guanidinate anion [hpp]$^-$ to form high oxidation-state niobium chloride complexes.

2. Experimental

2.1. General experimental procedures

All manipulations were carried out under dry nitrogen using standard Schlenk-line and cannula techniques, or in a conventional nitrogen-filled glovebox operating at <1 ppm oxygen. Solvents were dried over the appropriate drying agent and degassed prior to use. The reagents hppH (Fluka), NbCl$_5$ (Aldrich), ^{n}BuLi (2.5 M in hexanes, Acros) and SiMe$_3$Cl (Aldrich) were purchased from commercial sources and used as received. The compound hppSiMe$_3$ was synthesised according to the literature procedures and was used without further purification [18]. NMR spectra were recorded using a Bruker Avance DPX 300 MHz spectrometer at 300 (^{1}H) and 75 (^{13}C{^{1}H}) MHz. Proton and carbon chemical shifts were referenced internally to residual solvent resonances. Elemental analyses were performed by S. Boyer at London Metropolitan University.

2.1.1. Nb(hpp)Cl$_4$ (**1**)
2.1.1.1. Method 1. ^{n}BuLi (1.44 mL of a 2.5 M solution in hexane, 3.6 mmol) was added to a solution of hppH (0.50 g, 3.6 mmol) in THF at 0 °C. The solution was allowed to warm to room temperature and stirred for 1 h, after which time the solvent was removed to afford a white powder of the lithium salt, 'hppLi(THF)$_n$'. This product was slurried in toluene and added to a solution of NbCl$_5$ (0.97 g, 3.6 mmol) in toluene at −78 °C. After stirring at ambient temperature for 20 h, the volatile components were removed and the product extracted with dichloromethane. Removal of the volatiles afforded crude **1** as a brown solid. Yield 0.24 g, 18% (see Fig. 1).
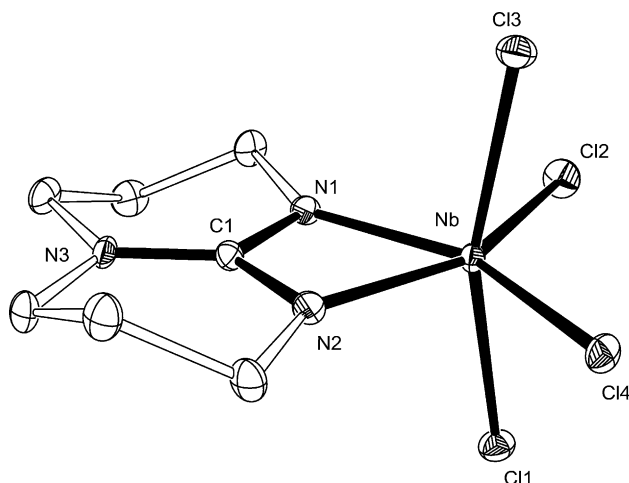
Fig. 1. ORTEP representation of Nb(hpp)Cl$_4$ (1) with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms omitted for clarity.

2.1.1.2. Method 2. A CH$_2$Cl$_2$ solution of hppSiMe$_3$ (0.76 g, 3.6 mmol) was added to a slurry of NbCl$_5$ (0.97 g, 3.6 mmol) in the same solvent, resulting in the instant formation of a deep red solution. Removal of the volatiles afforded crude 1 as a brown solid. Yield 0.49 g, 37%.

X-ray quality single crystals were obtained by layering a concentrated dichloromethane solution of 1 with diethyl ether at room temperature. Despite repeated attempts, accurate analysis could not be obtained on this compound due, we believe, to high oxygen/moisture sensitivity.

^{1}H NMR (CDCl$_3$, 298 K): δ 4.42, (m, 4H, C*H*$_2$), 3.47 (m, 4H, C*H*$_2$), 2.14 (m, 4H, C*H*$_2$). ^{13}C NMR (CDCl$_3$, 298 K): δ,[2] 50.5 (*C*H$_2$), 46.1 (*C*H$_2$), 21.6 (*C*H$_2$). Mass spectrum (EI$^+$, m/z): 336 [M − Cl]$^+$.

2.1.2. Nb(hpp)Cl$_4$(MeCN) (1a)

A solution of hppH (0.50 g, 3.6 mmol) in THF was cooled to 0 °C and 1 equiv of ^{n}BuLi (2.5 M solution in hexane) was added. The solution was allowed to warm to room temperature and stirred for 1 h, after which time the solvent was removed to afford a white solid. This product was dissolved in acetonitrile and added to a solution of NbCl$_5$ (0.97 g, 3.6 mmol) in acetonitrile at −78 °C. The resultant mixture was allowed to attain ambient temperature and was stirred for a further 20 h, after which time the volatile components were removed and the product extracted with acetonitrile. Removal of the solvent afforded crude 1a as a brown solid. Yield 0.30 g, 21%. Analytically pure samples were obtained by layering a concentrated acetonitrile solution of 1a with diethyl ether at 4 °C.

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[2] Quaternary *C*N$_3$ carbon atom not observed due to low solubility of the complex.

Anal. Calc. for C$_9$H$_{15}$Cl$_4$N$_4$Nb: C, 26.1; H, 3.6; N, 13.6%. Found: C, 26.4; H, 3.8; N, 13.4%. ^{1}H NMR (D$_5$-pyridine, 298 K): δ 3.02 (m, 4H, C*H*$_2$), 2.98 (m, 4H, C*H*$_2$), 1.83 (s, 3H, C*H*$_3$CN), 1.61 (m, 4H, C*H*$_2$). ^{13}C NMR (D$_5$-pyridine, 298 K): δ 151.5 (*C*N$_3$), 117.3 (CH$_3$*C*N), 46.5 (*C*H$_2$), 37.8 (*C*H$_2$), 20.5 (*C*H$_2$), 0.9 (*C*H$_3$CN). Mass spectrum (EI$^+$, m/z): 336 [M − Cl − MeCN]$^+$.

2.1.3. Nb(hpp)$_2$Cl$_3$ (2)

This compound was made using the procedure outlined for compound 1 (Method 1), using ^{n}BuLi (1.44 mL of a 2.5 M solution in hexane, 3.6 mmol), hppH (0.50 g, 3.6 mmol) and NbCl$_5$ (0.48 g, 1.8 mmol). Removal of the volatiles afforded crude 2 as a brown solid. Yield 0.21 g, 25%. X-ray quality single crystals were obtained by layering a concentrated dichloromethane solution of 2 with diethyl ether at room temperature.

Anal. Calc. for C$_{14}$H$_{24}$Cl$_3$N$_6$Nb: C, 35.3; H, 5.1; N, 17.7%. Found: C, 35.2; H, 5.2; N, 17.4%. ^{1}H NMR (CDCl$_3$, 298 K): δ 4.15, (m, 4H, C*H*$_2$), 3.40 (m, 4H, C*H*$_2$), 2.01 (m, 4H, C*H*$_2$). ^{13}C NMR (CDCl$_3$, 298 K): δ 165.1 (*C*N$_3$), 46.7 (*C*H$_2$), 46.2 (*C*H$_2$), 22.0 (*C*H$_2$). Mass spectrum (EI$^+$, m/z): 439 [M − Cl]$^+$.

2.1.4. Crystallography

Details of the crystal data, intensity collection and refinement are listed in Table 1. Crystals were covered in oil and suitable single crystals were selected under a microscope and mounted on a Kappa CCD diffractometer. The structures were refined with SHELXL-97 [19]. Additional features are listed below:

Nb(hpp)Cl$_4$(MeCN) (1a): The molecule lies on a crystallographic mirror plane. The hydrogen atoms of the MeCN ligand were not located due to rotational disorder.

3. Results and discussion

A solution of the neutral guanidine, hppH, in THF is readily deprotonated using ^{n}BuLi to afford the lithium salt, 'hppLi(THF)$_n$,' as a colourless to pale yellow solution. It has been shown by ourselves and others that this reagent may be used in situ (assuming quantitative conversion) allowing access to Y [7], Ti [8,9] and Sn [5] compounds. In the report detailed here, however, it proved necessary to avoid the use of THF solutions of the lithium salt during reaction with NbCl$_5$ due to the observed formation of viscous solutions arising from ring-opening polymerisation of the solvent.

To circumvent this problem, two approaches have been adopted. Isolation of the Li-salt by removal of the volatiles and reaction of a suspension of the off-white solid with niobium(V) chloride in toluene resulted in formation of the target product. This reaction

Table 1
Crystal structure and refinement data for Nb(hpp)Cl$_4$ (1), Nb(hpp)Cl$_4$(MeCN) (1a) and Nb(hpp)$_2$Cl$_3$ (2)

	1	1a	2
Formula	C$_7$H$_{12}$Cl$_4$N$_3$Nb	C$_9$H$_{15}$Cl$_4$N$_4$Nb	C$_{14}$H$_{24}$Cl$_3$N$_6$Nb
Formula weight	372.91	413.96	475.65
Temperature (K)	173(2)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal size (mm)	0.1 × 0.1 × 0.05	0.3 × 0.3 × 0.1	0.3 × 0.2 × 0.05
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	Fdd2 (No. 43)	Pnma (No. 62)	P2$_1$/c (No. 14)
Unit cell dimensions			
a (Å)	20.6984(5)	14.6905(4)	8.9352(2)
b (Å)	22.5968(6)	11.6199(3)	14.5828(3)
c (Å)	10.6567(3)	8.5313(2)	14.8878(3)
β (°)	90	90	103.291(1)
V (Å^3)	4984.3(2)	1456.31(6)	1877.92(7)
Z	16	4	4
D$_{calc}$ (mg/m^3)	1.99	1.89	1.67
Absorption coefficient (mm^{-1})	1.79	1.55	1.07
θ range for data collection (°)	3.94 to 25.03	4.06–27.88	3.71–30.02
Reflections collected	10307	8786	20278
Independent reflections (R$_{int}$)	2163 (0.052)	1808 (0.055)	5465 (0.053)
Reflections with I > 2σ(I)	2002	1528	4351
Data/restraints/parameters	2163/1/136	1808/0/94	5465/0/277
Goodness-of-fit on F^2	1.025	1.079	1.017
Final R indices [I > 2σ(I)]	R$_1$ = 0.029, wR$_2$ = 0.055	R$_1$ = 0.032, wR$_2$ = 0.068	R$_1$ = 0.036, wR$_2$ = 0.070
R indices (all data)	R$_1$ = 0.035, wR$_2$ = 0.058	R$_1$ = 0.043, wR$_2$ = 0.073	R$_1$ = 0.053, wR$_2$ = 0.077
Largest different peak and hole	0.36 and −0.42	0.65 and −0.50	0.67 and −0.60

proceeds despite the likely retention of THF as solvate molecules in the lithium reagent, but may be one of the contributory factors to the low observed yield of this reaction. Alternatively, generating the silylated species, hppSiMe$_3$ [18], by quenching the lithium salt with trimethylsilylchloride and reacting the unpurified silyl reagent with niobium(V) chloride was also demonstrated to afford the targeted niobium guanidinate complex via elimination of trimethylsilylchloride.

The 1:1 reaction between 'hppLi' or hppSiMe$_3$ and NbCl$_5$, in toluene or CH$_2$Cl$_2$, respectively, proceeded with the formation of a brown/red solution. After the appropriate work-up, crystals of the pure compound, Nb(hpp)Cl$_4$ (1) were obtained by layering a concentrated CH$_2$Cl$_2$ solution with Et$_2$O (Scheme 2). Alternatively, replacing the THF with MeCN during ligand metathesis with the lithium salt resulted in isolation of the mono-acetonitrile adduct Nb(hpp)Cl$_4$(MeCN) (1a). Using an analogous approach and changing the stoichiometry afforded the bis-ligand species, Nb(hpp)$_2$Cl$_3$ (2). The low yields of these compounds (typically <40%) may be due to partial reduction when employing the lithium reagents, as observed previously with the acyclic guanidinate [(Me$_3$Si)$_2$NC{NCy}$_2$]$^-$ [17]. The low solubility of these species also resulted in loss of material during the purification procedures.

The ^{1}H NMR spectra for each compound was commensurate with a symmetrically bound guanidinate, as indicated by three sets of multiplets corresponding to the equivalent methylene groups within the bicyclic

framework. All other data were in agreement with the formulated structures. However, despite repeated attempts, accurate analysis could not obtained for compound 1. Examination of the crystal structure of this compound indicates a highly exposed metal centre which is predicted to be very reactive to atmospheric oxygen/moisture (vide infra). Single crystal X-ray diffraction analyses have been performed on each of the compounds; crystal structure and refinement data are

Table 2
Selected bond lengths (Å) for Nb(hpp)Cl$_4$ (1), Nb(hpp)Cl$_4$(MeCN) (1a) and Nb(hpp)$_2$Cl$_3$ (2)

1			
Nb–N(1)	2.049(4)	Nb–Cl(1)	2.3836(13)
Nb–N(2)	2.046(4)	Nb–Cl(2)	2.3437(13)
C(1)–N(1)	1.352(6)	Nb–Cl(3)	2.3862(13)
C(1)–N(2)	1.361(6)	Nb–Cl(4)	2.3494(12)
C(1)–N(3)	1.303(5)		
1a			
Nb–N(1)	2.069(2)	Nb–Cl(1)	2.365(1)
Nb–N(3)	2.330(4)	Nb–Cl(2)	2.4495(7)
C(1)–N(1)	1.346(3)	Nb–Cl(3)	2.390(1)
C(1)–N(2)	1.311(5)		
2			
Nb–N(1)	2.119(2)	Nb–Cl(1)	2.4513(6)
Nb–N(2)	2.078(2)	Nb–Cl(2)	2.4223(6)
Nb–N(4)	2.116(2)	Nb–Cl(3)	2.4493(7)
Nb–N(5)	2.125(2)	C(1)–N(1)	1.344(3)
C(8)–N(4)	1.337(3)	C(1)–N(2)	1.343(3)
C(8)–N(5)	1.351(3)	C(1)–N(3)	1.325(3)
C(8)–N(6)	1.327(3)		

32000

collected in Table 1 and selected bond lengths and angles in Tables 2 and 3, respectively.

Compound **1** consists of a distorted octahedral niobium centre, with the smallest angle [64.11(14)°] corresponding to the bite angle of the chelating ligand within the four-membered metallacycle. Of particular note is the large Cl–Nb–Cl angle located in the ligand plane [122.42(5)°] which is ∼35° more obtuse than the remaining intramolecular chloride angles [range 85.57(4)–86.39(5)°]. This exceptionally large angle results in a sterically accessible niobium centre (**B** and **C**, Fig. 2) which, coupled with the electron deficient niobium centre renders the complex highly susceptible to interaction with donor molecules. Whilst we believe that this feature is responsible for the high moisture/oxygen

sensitivity of the complex, the facile access to the metal may be advantageous in catalytic applications, where metal···substrate interactions are frequently associated with key steps within a catalytic cycle.

Examination of the bond distances within the guanidinate suggest a significant contribution from the zwitterionic resonance structure [**A**, Scheme 1] to the overall bonding. Thus, the C(1)–N(3) distance [1.303(5) Å] is indicative of considerable double bond character, being much shorter than the remaining two carbon–nitrogen bonds [ave. 1.357(6) Å]. We have previously defined the parameter Δ'_{CN} as the difference between the average C–N$_{amidine}$ and C–N$_{amide}$ bond lengths [9], where the resultant value may be used as a qualitative measure of the extent to which the nitrogen lone pair of the amide group is involved in the bonding. Totally symmetrical delocalisation throughout the 'CN$_3$' moiety would give result in $\Delta'_{CN} = 0$, and increasingly positive values suggest greater contribution from **A**. For compound **1**, the relatively large value of Δ'_{CN} [0.054 Å] is indicative of asymmetric distribution of π-electron density with a short C–N$_{amide}$ bond distance, commensurate with an electron-deficient niobium centre. In agreement with this model, the resultant Nb–N distances [ave. 2.048(4) Å] are short compared to the corresponding metal–ligand distances in the other compounds within this study (vide infra).

As a proof of concept that the exposed metal centre in **1** would be susceptible to interaction with donor molecules, and to investigate the effects of changing the electron density and coordination number on the bonding parameters, we also report the molecular structure of the acetonitrile adduct, Nb(hpp)Cl$_4$(MeCN), **1a**. In this structure, the niobium has expanded its coordination sphere to a seven-coordinate, distorted pentagonal bipyramid in which the guanidinate, acetonitrile and two of the chloride are equatorially positioned and the remaining two chloride ions are axial. As predicted from the structure of **1**, the acetonitrile is located between the two chlorides that previously defined the largest angle in

Table 3
Selected angles (°) for compounds Nb(hpp)Cl$_4$ (**1**), Nb(hpp)Cl$_4$(MeCN) (**1a**) and Nb(hpp)$_2$Cl$_3$ (**2**)

| **1**			
N(1)–Nb–N(2)	64.11(14)	Cl(1)–Nb–Cl(2)	85.69(5)
N(1)–Nb–Cl(1)	98.81(11)	Cl(1)–Nb–Cl(4)	86.08(4)
N(1)–Nb–Cl(2)	88.32(11)	Cl(2)–Nb–Cl(3)	86.39(5)
N(1)–Nb–Cl(3)	95.90(11)	Cl(2)–Nb–Cl(4)	122.42(5)
N(2)–Nb–Cl(1)	96.84(11)	Cl(3)–Nb–Cl(4)	85.57(4)
N(2)–Nb–Cl(3)	97.11(11)		
N(2)–Nb–Cl(4)	85.17(11)		
1a			
N(1)–Nb–N(1′)	62.90(13)	N(1)–Nb–Cl(1)	93.20(8)
N(1)–Nb–Cl(2)	76.77(7)	N(1)–Nb–Cl(3)	93.28(8)
N(3)–Nb–Cl(1)	80.50(10)	N(3)–Nb–Cl(2)	72.27(2)
N(3)–Nb–Cl(3)	91.90(11)	Cl(1)–Nb–Cl(2)	92.07(2)
Cl(2)–Nb–Cl(3)	85.56(2)	[Cl(2)–Nb–Cl(2′)	143.05(4)]
2			
N(1)–Nb–N(2)	62.57(8)	N(4)–Nb–N(5)	62.11(8)
N(1)–Nb–N(5)	78.60(8)	N(2)–Nb–Cl(1)	78.96(6)
N(4)–Nb–Cl(1)	79.13(6)	N(1)–Nb–Cl(2)	84.32(6)
N(2)–Nb–Cl(2)	94.01(6)	N(4)–Nb–Cl(2)	91.45(6)
N(5)–Nb–Cl(2)	94.54(6)	N(1)–Nb–Cl(3)	95.97(6)
N(2)–Nb–Cl(3)	86.70(6)	N(4)–Nb–Cl(3)	87.90(6)
N(5)–Nb–Cl(3)	84.89(6)	Cl(1)–Nb–Cl(2)	88.64(2)
Cl(1)–Nb–Cl(3)	91.54(2)		
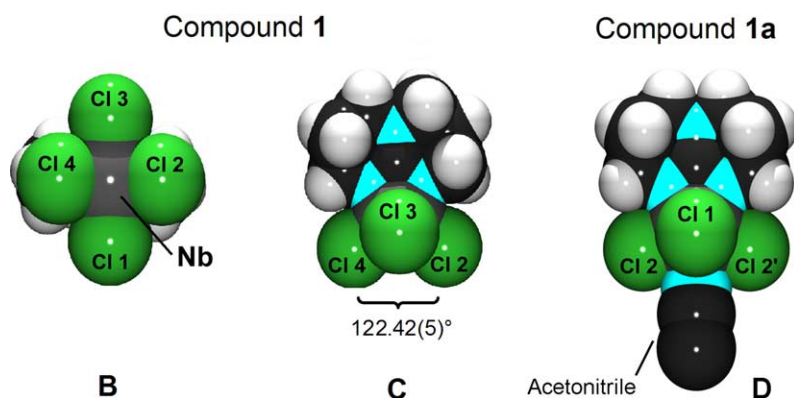
Fig. 2. Spacefilling representations of compound **1** (perpendicular views **B** and **C**), illustrating the exposed niobium centre, and compound **1a** (**D**) showing coordination of the acetonitrile molecule.
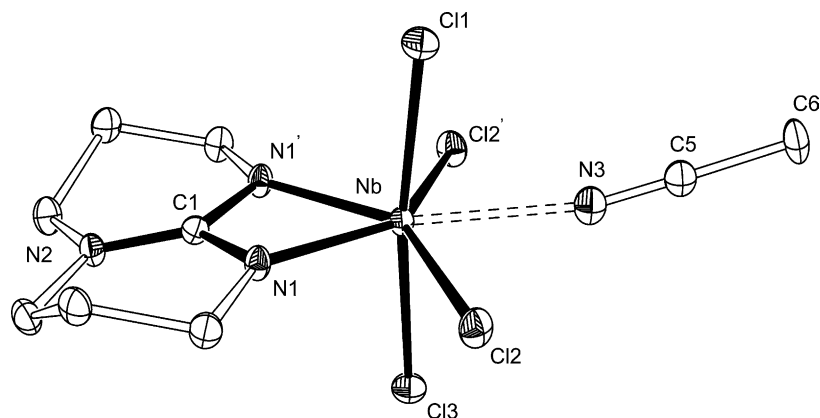
Fig. 3. ORTEP representation of Nb(hpp)Cl₄(MeCN) (**1a**) with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms omitted for clarity.

the base-free compound. The resultant distribution of angles about the equatorial plane is in the range 62.90(13)° [bite angle of the ligand] to 76.77(7)° (see Fig. 3).

The incorporation of a donor acetonitrile molecule in the coordination sphere increases the electron density at the metal, which in turn effects the delocalisation of π-electrons in the ligand. The C(1)–N(2) distance [1.311(5) Å] is indistinguishable from the corresponding distance in **1**, again suggesting a large contribution from resonance form **A**. The Δ'_{CN} value [0.035 Å] does, however, represent a bonding situation closer to symmetrical delocalisation throughout the 'CN₃' moiety of the ligand, implying that the electron density at the metal plays an important role in determining the extent to which the zwitterionic resonance contributes to the overall bonding. The longer Nb–N distance [2.069(2) Å], is at the limit of being statistically distinguishable from the corresponding metal–ligand distance in **1**, but is in general agreement with the electronic reasoning presented above. We acknowledge, however, that such arguments can never be completely disengaged from steric considerations and recognise that **1a** consists of a more crowded, seven-coordinate niobium centre.

To further probe the structural parameters of niobium-hpp compounds, the bis-ligand compound, Nb(hpp)₂Cl₃ (**2**) was analysed using X-ray diffraction techniques. The compound consists of a monomeric, seven-coordinate distorted pentagonal niobium in which both ligands chelate in the equatorial plane and two of the chlorides are located axially. The ligand bite angles [62.11(8)° and 62.57(8)°] are in the expected range for this type of bonding mode, representing the smallest angles about the equatorial plane [range = 62.11(8)–79.13(6)°] (see Fig. 4).

The bond lengths within the ligands show a further decrease in the extent to which **A** contributes to the bonding, with Δ'_{CN} values of 0.019 and 0.018 Å. The Nb–N distances reflect this trend, being on average sig-
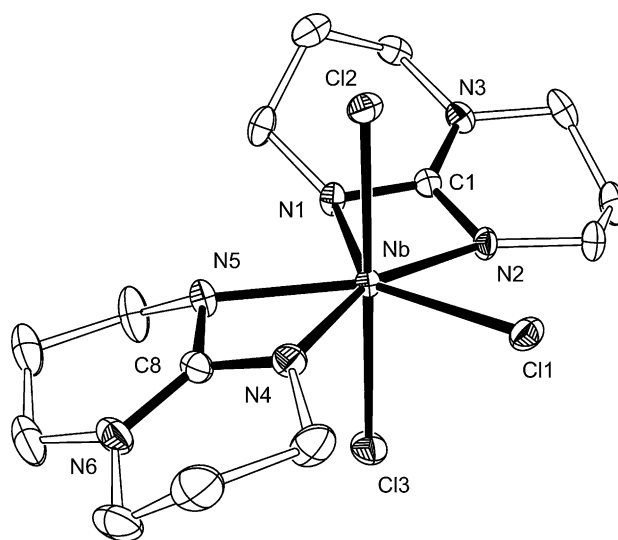

Fig. 4. ORTEP representation of Nb(hpp)₂Cl₃ (**2**) with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms omitted for clarity.

nificantly longer than in either of the previous two examples [ave. 2.109(2) Å]. Once again the different steric environments about the metal must also be taken into account when considering these values.

4. Conclusions

We have demonstrated that the 'electron-rich' guanidinate, [hpp]⁻, is a suitable ligand for the stabilisation of niobium in oxidation state +5. Synthetic routes to these compounds using lithium reagents are typically low yielding which may reflect reductive processes occurring during the reaction. The mono-ligand species may be isolated as a highly sensitive, base-free complex, and analysis of the X-ray diffraction data reveals a highly exposed metal centre. Accordingly the formation of the

acetonitrile adduct was observed, where the donor molecule is located in the equatorial plane of a distorted pentagonal bipyramid. The bis-ligand compound was shown by crystallography to have a similar geometry about a seven-coordinate niobium, where both ligands chelate in the equatorial plane. Examination of the bond lengths within the ligand indicate that increasing the electron density at the metal reduces the extent to which the lone-pair of the amide nitrogen is delocalised into the ligand framework. A concomitant increase in the metal–ligand bond distance is observed, although steric factors are also involved in the determination of this parameter.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 262415–262417 for compounds **1**, **1a** and **2**. 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; email: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

Acknowledgements

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[2] The authors also wish to mention the extensive work of Cotton and co-workers in the application of the [hpp]⁻ anion in the support of multiply bonded metal species. We feel however that such work is outside of the remit of the current article..

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