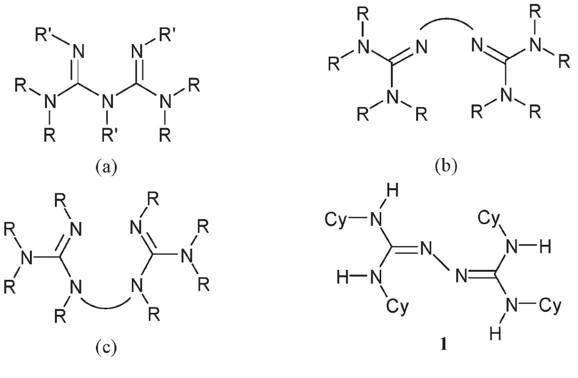
The first urea azine molecule and its coordination to uranium in the first actinide guanidinate complexes

Claude Villiers, Pierre Thuéry and Michel Ephritikhine*

Received (in Cambridge, UK) 5th April 2007, Accepted 5th June 2007
First published as an Advance Article on the web 18th June 2007
DOI: 10.1039/b705224c

The urea azine molecule $(CyNH)_2C{=}N{-}N{=}C(HNCy)_2$ (1) was easily prepared by reaction of the carbodiimide $CyN{=}C{=}NCy$ and H_2NNH_2 and this novel type of bis-guanidine proved useful in affording chelating and bridging ligands for the building of polynuclear compounds, as illustrated by the synthesis of the first uranium guanidinate complexes $[(THF)_2Li(\mu\text{-}Cl)_2UCl(\mu\text{-}L)]_2$ (2) and $[UCl(\mu\text{-}L)_2UCl_2(\mu\text{-}Cl)_2UCl(\mu\text{-}L)]_2$ (3) (L = 1 − 2H); the X-ray crystal structures of compounds 1–3 were determined.

Guanidines and their anions are sterically and electronically flexible ancillary ligands which endow a variety of metal complexes with interesting structures and reactions.[1,2] A special attention has been paid to biguanidines and also, more recently, to bis-guanidines (Scheme 1) wherein both guanidine subunits are connected *via* either the N_{amine} or N_{imine} atoms by an organic bridge; these bifunctional and chelating ligands were designed for controlling and improving the properties of the complexes, in particular in their applications in catalysis and biomimetic coordination chemistry.[3–5] These linked bis-guanidines have been so far used as neutral ligands, with the exception of $CH_2CH_2[N{=}C(NH^iPr)_2]_2$ which is found as a bis-guanidinate ligand in some mononuclear titanium and zirconium complexes.[6] Here we present the synthesis and crystal structure of the first bis-guanidine in which the two CN_3 functionalities are directly connected by a N_{imine}–N_{imine} bond, $(CyNH)_2C{=}N{-}N{=}C(HNCy)_2$ (**1**), namely the azine of the dialkyl urea $(CyNH)_2C{=}O$ (Scheme 1).


(a) (b) (c) 1

Scheme 1 Biguanidines (a), linked bis-guanidines (b) and (c), and the urea azine **1**.

In view of the number and variety of guanidinate complexes of d transition metals and lanthanides, it is surprising that no such compound of a 5f-element was reported. Molecule **1** served to synthesize the tetra- and hexanuclear uranium complexes $[(THF)_2Li(\mu\text{-}Cl)_2UCl(\mu\text{-}L)]_2$ and $[UCl(\mu\text{-}L)_2UCl_2(\mu\text{-}Cl)_2UCl(\mu\text{-}L)]_2$ (L = **1** − 2H) whose crystal structures evidence the chelating and bridging capacity of the bis-guanidinate ligand.

Compound **1** was isolated in quantitative yield from the reaction of *N,N′*-dicyclohexylcarbodiimide and 0.5 mol. equivalent of hydrazine monohydrate in THF at 20 °C.† While addition of amines to carbodiimides constitutes a classical route to guanidines, reactions of hydrazines and carbodiimides seem to have been neglected; although it was reported in 1902 that the bis-guanidine prepared from $PhN{=}C{=}NPh$ and H_2NNH_2 readily undergoes intramolecular cyclization with elimination of aniline to form the related substituted 1,2,4-triazole,[7] the other reactions are limited, to the best of our knowledge, to the preparation of amino-imidazolones after cyclization of the likely guanidine intermediate,[8] and acid-catalyzed reactions in DMSO which did not afford guanidines but complex mixtures of products.[9]

A view of **1** is shown in Fig. 1 together with selected bond lengths and angles.‡ The molecule adopts a centrosymmetric *trans*

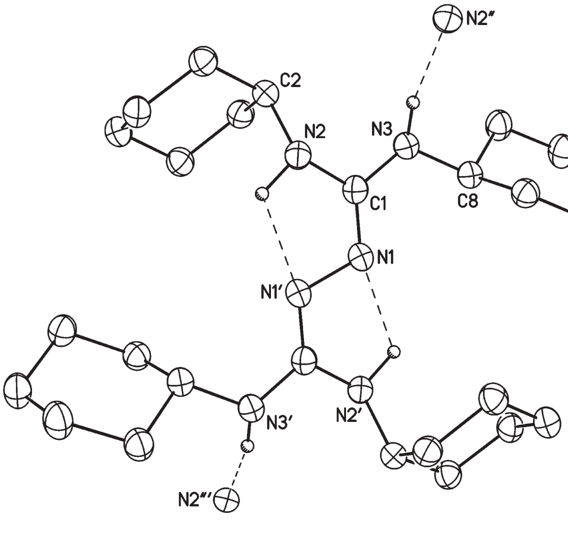
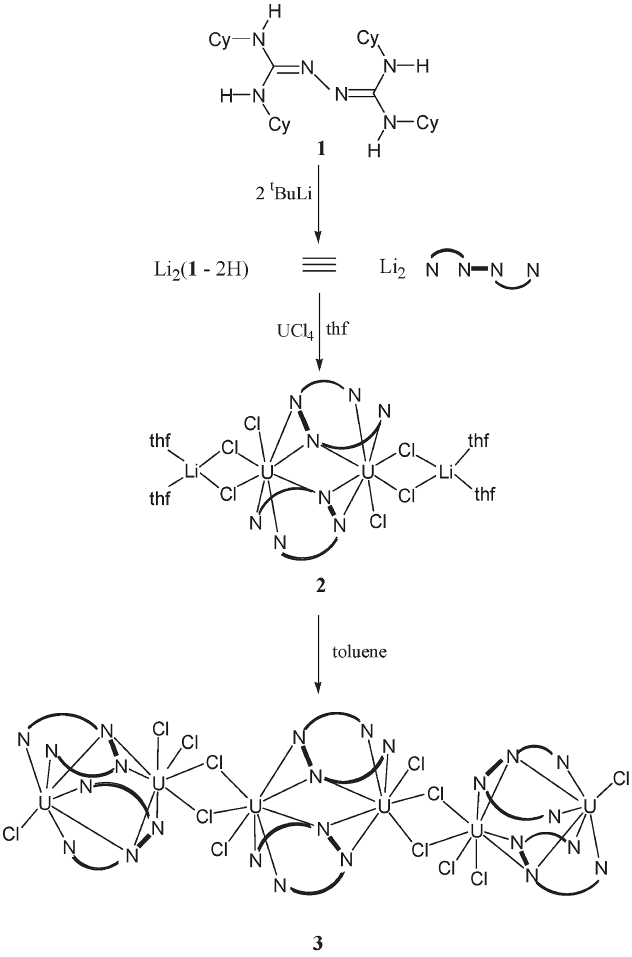


Fig. 1 View of **1**. Hydrogen atoms of the Cy groups have been omitted. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines. Selected bond lengths (Å) and angles (°): C1–N1 1.2971(15), C1–N2 1.4004(14), C1–N3 1.3809(14), N1–N1′ 1.4290(18), N1–C1–N2 123.88(10), N2–C1–N3 115.13(10), N1–C1–N3 120.98(10), C1–N1–N1′ 111.46(11). Symmetry codes: ′ = 1 − *x*, −*y*, −*z*; ″ = 1 − *x*, *y*, −*z* + ½, ‴ = *x*, −*y*, *z* − ½.

Service de Chimie Moléculaire, DSM, DRECAM, CNRS URA 331, Laboratoire Claude Fréjacques, CEA Saclay, Bâtiment 125, 91191, Gif-sur-Yvette, France. E-mail: claude.villiers@cea.fr; michel.ephritikhine@cea.fr; Fax: +33 169 08 66 40; Tel: +33 169 08 64 36

configuration with the two CN_3 units essentially planar (r.m.s. deviation 0.029 Å). The N1–N1′ and C1–N1 distances are characteristic of a single and double bond, respectively; the C–N, C=N and N–N distances in the NH–C=N–N=C–NH fragment can be compared with the corresponding parameters in the picolinamide azine [1.345(3), 1.291(5) and 1.424(3) Å][10] and other related ligands.[11,12] The configuration adopted by **1** involves an intramolecular hydrogen bond between N2 and N1′ [N2···N1′ 2.6103(13) Å, N2–H2···N1′ 112°] while N3 is involved in an intermolecular hydrogen bond with the N2 atom of the neighbouring molecule [N3···N2″ 3.1864(14) Å, N3–H3···N2″ 161°], resulting in the formation of hydrogen bonded chains parallel to the *c* axis.

Successive treatment of **1** with 2 mol. equivalents of ^{t}BuLi and 1 mol. equivalent of UCl_4 in THF gave a green solution, and addition of pentane led to the formation of green crystals of $[(THF)_2Li(\mu\text{-}Cl)_2UCl(\mu\text{-}L)]_2$ (**2**) (L = **1** − 2H) which were contaminated with LiCl (Scheme 2). The mixture of **2** and LiCl was extracted with toluene and after the lithium salt was eliminated by filtration, the solution deposited green-brown crystals of $[UCl(\mu\text{-}L)_2UCl_2(\mu\text{-}Cl)_2UCl(\mu\text{-}L)]_2$ (**3**) in 95% yield upon addition of pentane.† Complexes **2** and **3** are assemblies of $LUCl_2$ units.



Scheme 2 Synthesis of the complexes.

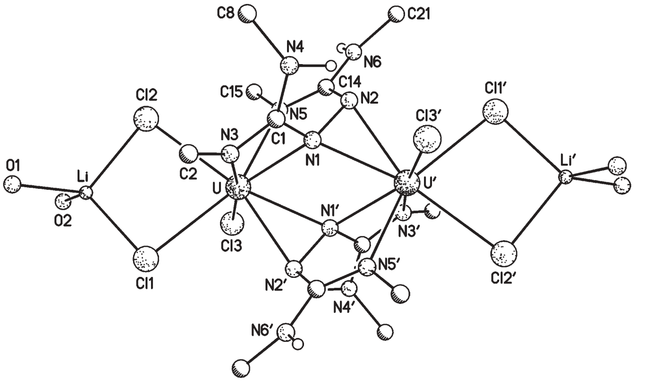


Fig. 2 View of **2**. The carbon and hydrogen atoms of the Cy groups and THF molecules have been omitted and all atoms are represented as spheres of arbitrary radii for clarity. Selected bond lengths (Å): U–N1 2.438(3), U–N3 2.491(3), U–N5 2.399(3), U–N1′ 2.449(3), U–N2′ 2.402(3), U–Cl1 2.8148(9), U–Cl2 2.8038(9), U–Cl3 2.6845(9), C1–N1 1.376(5), C1–N3 1.312(4), C1–N4 1.379(4), C14–N2 1.369(4), C14–N5 1.344(4), C14–N6 1.353(4), N1–N2 1.449(4). Symmetry code: ′ = 1 − *x*, −*y*, −*z*.

In the centrosymmetric structure of **2** (Fig. 2),‡ the two metal centres are bridged by the N1 atom of the bis-guanidinate ligand which is also attached to U *via* N3 and N5 and to U′ *via* N2; the two CN_3 functionalities involving C1 and C14 thus adopt respectively a $\mu{:}\eta^3$ and $\mu{:}\eta^2$ ligation mode. The U–N distances are in the range 2.399(3)–2.491(3) Å with an average value of 2.44(3) Å which can be compared with those of 2.417(7) Å in the oxalamidinate $[Li(py)_4]_2[\{UCl_4(py)\}_2(\mu\text{-}C_2N_4Cy_4)]$[13] and 2.43(4) Å in the trisamidinate $U[MeC(NCy)_2]_3Cl$.[14] The N1–N2 distance of 1.449(4) Å is characteristic of a single bond while the C1–N and C14–N distances vary from 1.312(4) to 1.379(4) Å and average 1.36(2) Å, showing the electronic delocalization over each CN_3 unit; however, the short C1–N3 and long C1–N1 and C1–N4 bonds indicate that N3 has a strong imine character, in keeping with the U–N3 bond being larger than the others. The N4 and N6 atoms, which are not coordinated to the metal, are protonated. The uranium atom completes its coordination sphere with three chlorine atoms, two of those being in bridging position between the U and Li atoms, and the uranium environment can be seen as a distorted square antiprism defined by the square bases N1–N3–Cl2–N5 and N1′–N2′–Cl1–Cl3 (r.m.s. deviations 0.009 and 0.258 Å respectively) forming a dihedral angle of 4.96(12)°. The U–Cl distances and the geometrical parameters of the tetrahedral Li atom are unexceptional.

The structure of the hexanuclear complex **3** is also centrosymmetric (Fig. 3). The geometry of the central dinuclear fragment (which contains U3 and the ligand labelled C associated to their images by symmetry) is quite identical to that found in **2**, with very similar metrical parameters. In the lateral dinuclear moiety, the guanidinate ligands A and B adopt the same bridging ligation mode as ligand C but both chelate the same uranium atom U1 *via* the N1, N3 and N5 atoms and are coordinated to U2 *via* N1 and N2. The lateral and central dinuclear fragments are bridged by the Cl4 and Cl5 atoms, and the coordination spheres of U1 and U2 are completed by one and two chloride ligands, respectively. The seven-coordinate U1 atom can be seen to be in a very distorted capped trigonal prismatic environment with the trigonal faces N1A–N3A–N5A and N1B–N3B–N5B forming a dihedral angle of 19.9(7)° and the Cl1 atom in capping position, while the configuration of U2 is distorted square antiprismatic, with the

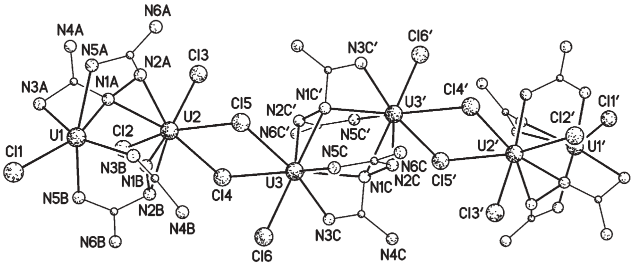


Fig. 3 View of **3**. The carbon atoms of the Cy groups and the hydrogen atoms have been omitted and all atoms are represented as spheres of arbitrary radii for clarity. Selected bond lengths (Å): U1–N1A 2.411(11), U1–N3A 2.460(12), U1–N5A 2.379(11), U1–N1B 2.437(10), U1–N3B 2.455(10), U1–N5B 2.331(13), U1–Cl1 2.645(4), U2–N1A 2.389(10), U2–N2A 2.444(11), U2–N1B 2.444(12), U2–N2B 2.391(11), U2–Cl2 2.631(4), U2–Cl3 2.633(3), U2–Cl4 2.786(3), U2–Cl5 2.774(3), U3–N1C 2.428(9), U3–N3C 2.446(9), U3–N5C 2.401(9), U3–N1C′ 2.465(10), U3–N2C′ 2.392(9), U3–Cl4 2.846(3), U3–Cl5 2.821(3), U3–Cl6 2.668(3). Symmetry code: ′ = 1 − *x*, 1 − *y*, −*z*.

square bases N1A–N2A–Cl2–Cl3 and N1B–N2B–Cl4–Cl5 (r.m.s. deviations 0.109 and 0.103 Å respectively) forming a dihedral angle of 5.5(3)°. The U3 atom is also in a square antiprismatic environment defined by the square bases N1C–N3C–N5C–Cl6 and N1C′–N2C′–Cl4–Cl5 (r.m.s. deviations 0.0015 and 0.18 Å respectively) which form a dihedral angle of 7.1(4)°. The separation between the uranium atoms in the asymmetric dinuclear fragment of **3** [U1···U2 3.9304(9) Å] is smaller than in the centrosymmetric fragments of both **3** and **2** [U3···U3′ 4.0609(11) Å and U···U′ 4.1304(3) Å, respectively].

In conclusion, the synthesis of **1** shows that carbodiimides can be easily transformed into urea azines by reaction with hydrazine. This novel type of bis-guanidine molecule offers useful chelating and bridging ligands for the building of polynuclear compounds, as illustrated by the synthesis of the first uranium guanidinate complexes.

Notes and references

† *Synthesis and characterizing data*. All manipulations were carried out under argon, except for compound **1**, which is air-stable. Compound **1**: A flask was charged with *N*,*N*′-dicyclohexylcarbodiimide (1.64 g, 7.95 mmol) and hydrazine monohydrate (193 μL, 3.97 mmol) in THF (10 mL). After 48 h at 20 °C, the solution was evaporated to dryness, leaving the off-white powder of **1** in quantitative yield (1.770 g). Colorless crystals were obtained by slow evaporation of the solution. ^{1}H NMR (THF-d$_8$, 200 MHz): δ(ppm) 0.98–2.00 (m, 40H, Cy), 3.10 and 3.42 (m, 2H + 2H, Cy), 3.70 (d, *J* 7 Hz, 2H, NH), 5.72 (d, *J* 11 Hz, 2H, NH). IR: *ν*(N–H): 3263 (m); *ν*(C=N): 1606 (s). Anal. calc. for $C_{26}H_{48}N_6$: C, 70.22; H, 10.88; N, 18.90. Found: C, 70.07; H, 10.94; N, 19.02%. Compounds **2** and **3**: ^{t}BuLi (250 μL of a 1.7 M solution in THF, 0.425 mmol) was added into a solution of **1** (94.0 mg, 0.212 mmol) in THF (10 mL). After 2 h at 20 °C, UCl_4 (81.0 mg, 0.212 mmol) was added into the pale yellow solution and the reaction mixture was stirred for 3 h at 20 °C. Addition of pentane led to the formation of green crystals of **2** together with colorless crystals of LiCl. In another experiment, the reaction mixture was evaporated to dryness and the residue extracted with toluene (10 mL). After filtration, addition of pentane led to the formation of green-brown crystals of **3** (171 mg, 95%). No signal corresponding to the bis-guanidinate ligands are visible in the ^{1}H NMR spectra, certainly because of rapid exchange reactions; the spectra reveal the presence of toluene molecules which could occupy the voids observed in the crystal structure (*vide infra*). Anal. calc. for $C_{184}H_{308}Cl_{12}N_{36}U_6$ (**3**·4toluene): C, 45.30; H, 6.36; Cl, 8.72; N, 10.34. Found: C, 45.52; H, 6.58; Cl, 8.72; N, 10.18%.

‡ Crystal data for **1**: $C_{26}H_{48}N_6$, *M* = 444.70, monoclinic, space group *C*2/*c*, *a* = 15.1574(16), *b* = 17.4268(19), *c* = 12.5035(9) Å, *β* = 126.373(6)°, *V* = 2659.3(5) Å^3, *Z* = 4, *T* = 100(2) K. Refinement of 145 parameters on 2524 independent reflections out of 62798 measured reflections (R_{int} = 0.020) led to R_1 = 0.040, wR_2 = 0.104, *S* = 1.048, $\Delta\rho_{min}$ = −0.18, $\Delta\rho_{max}$ = 0.15 e Å^{-3}. Crystal data for **2**: $C_{68}H_{124}Cl_6Li_2N_{12}O_4U_2$, *M* = 1876.43, orthorhombic, space group *Pbca*, *a* = 16.2729(6), *b* = 21.7473(6), *c* = 22.4638(7) Å, *V* = 7949.8(4) Å^3, *Z* = 4, *T* = 100(2) K. Refinement of 424 parameters on 7519 independent reflections out of 157305 measured reflections (R_{int} = 0.040) led to R_1 = 0.031, wR_2 = 0.060, *S* = 1.019, $\Delta\rho_{min}$ = −0.75, $\Delta\rho_{max}$ = 0.52 e Å^{-3}. Crystal data for **3**: $C_{156}H_{276}Cl_{12}N_{36}U_6$, *M* = 4509.71, triclinic, space group $P\bar{1}$, *a* = 13.6490(18), *b* = 15.660(2), *c* = 25.593(4) Å, *α* = 78.538(7), *β* = 83.988(8), *γ* = 65.304(8)°, *V* = 4869.4(12) Å^3, *Z* = 1, *T* = 100(2) K. Refinement of 946 parameters on 18129 independent reflections out of 120010 measured reflections (R_{int} = 0.095) led to R_1 = 0.071, wR_2 = 0.177, *S* = 0.876, $\Delta\rho_{min}$ = −0.86, $\Delta\rho_{max}$ = 1.72 e Å^{-3}. Data were collected on a Nonius Kappa-CCD area-detector diffractometer and processed with HKL2000.[15] Absorption effects for **2** and **3** were corrected with the program SCALEPACK.[15] The structures were solved by direct methods and refined by full-matrix least-squares on F^2 with SHELXTL.[16] All non-hydrogen atoms were refined with anisotropic displacement parameters, with restraints on bond lengths and/or displacement parameters for some badly behaving atoms in **3** (particularly in the cyclohexane rings). The hydrogen atoms bound to nitrogen atoms in **1** and **2** were found on Fourier-difference maps and all other hydrogen atoms in all three compounds were introduced at calculated positions; all were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom. Large voids in the lattice of **3** indicate the presence of unresolved solvent molecules. CCDC 643701–643703. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b705224c

1 P. J. Bailey and S. Pace, *Coord. Chem. Rev.*, 2001, **214**, 91.
2 M. P. Coles, *Dalton Trans.*, 2006, 985.
3 S. Herres-Pawlis, A. Neuba, O. Seewald, T. Seshadri, H. Egold, U. Flörke and G. Henkel, *Eur. J. Org. Chem.*, 2005, 4879.
4 S. Herres-Pawlis, U. Flörke and G. Henkel, *Eur. J. Inorg. Chem.*, 2005, 3815.
5 S. H. Oakley, M. P. Coles and P. B. Hitchcock, *Inorg. Chem.*, 2004, **43**, 7564.
6 T. G. Ong, G. P. A. Yap and D. S. Richeson, *Organometallics*, 2003, **22**, 387.
7 M. Bush and T. Ulmer, *Ber. Dtsch. Chem. Ges.*, 1902, **35**, 1721.
8 J. Z. Yuan, B. Q. Fu, M. W. Ding and G. F. Yang, *Eur. J. Org. Chem.*, 2006, 4170.
9 U. Lerch and J. G. Moffatt, *J. Org. Chem.*, 1971, **36**, 3861.
10 Z. Xu, L. K. Thompson and D. O. Miller, *Inorg. Chem.*, 1997, **36**, 3985.
11 S. Patra, T. A. Miller, B. Sarkar, M. Niemeyer, M. D. Ward and G. K. Lahiri, *Inorg. Chem.*, 2003, **42**, 4707.
12 F. Palacios, M. Ledigo, I. Perez de Heredia, J. M. Ezpeleta and G. Rubiales, *Heterocycles*, 2001, **55**, 1641.
13 C. Villiers, P. Thuéry and M. Ephritikhine, *Chem. Commun.*, 2006, 392.
14 C. Villiers, P. Thuéry and M. Ephritikhine, *Eur. J. Inorg. Chem.*, 2004, 4624.
15 Z. Otwinowski and W. Minor, *Methods Enzymol.*, 1997, **276**, 307.
16 G. M. Sheldrick, SHELXTL, Version 5.1, Bruker AXS Inc., Madison, WI, USA, 1999.