

Hydrogen-Bonded Networks Featuring Yttrium(III) Complexes of N,N'-Dimethylurea (DMU): Preparation and Characterization of $[Y(DMU)_6][YCl_6]$ and $[Y(NO_3)_3(DMU)_3]$

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In dedication to Professor Herman O. Desseyn for his 65th birthday and for his important contributions to Coordination Chemistry and Vibrational Spectroscopy

In order to examine the possibility of using yttrium(III) in the crystal engineering of hydrogen-bonded coordination complexes and to compare the molecular and supramolecular Y^{III}/Cl^- or NO_3^-/DMU chemistry with the already well-developed Ln^{III}/Cl^- or NO_3^-/DMU chemistry (Ln^{III} = lanthanide, DMU = N,N'-dimethylurea), compounds $[Y(DMU)_6][YCl_6]$ (**1**) and $[Y(NO_3)_3(DMU)_3]$ (**2**) have been prepared. The structures of both compounds have been determined by single-crystal X-ray diffraction. The structure of **1** consists of octahedral $[Y(DMU)_6]^{3+}$ and $[YCl_6]^{3-}$ ions. The Y^{III} ion in **2** is nine-coordinate and ligation is provided by three O-bonded DMU ligands and three bidentate chelating nitrate groups; the coordination polyhedron about the metal can be viewed as a distorted, monocapped square antiprism. The $[Y(DMU)_6]^{3+}$ cations and $[YCl_6]^{3-}$ anions self-assemble to form a hydrogen-bonded 3D architecture in **1**. Most of the hydrogen-bonding functionalities on the components of **2** create also a 3D network. Two motifs of interionic/intramolecular hydrogen-bonds have been observed: $N-H \cdots Cl$ in **1** and $N-H \cdots O(NO_3^-)$ in **2**. The IR data are discussed in terms of the nature of bonding and the structures of the two complexes.

Key words: Crystal Structures, Hydrogen-Bonded Coordination Complexes, Vibrational Spectroscopy, Yttrium(III)/N,N'-Dimethylurea Complexes, Yttrium(III) Nitrate Complexes

Introduction

A synthetic strategy currently employed in metallo-supramolecular chemistry utilizes ligands that can coordinate to a metal ion through a primary coordination site, while at the same time participate in additional bonding interactions at peripheral sites [1–3]. These supplementary sites may propagate weaker secondary connections (first approach), mainly *via* hydrogen-bonding [4–6], or may act as exodentate sites allowing further metal ion coordination and leading to coordination polymers (second approach) [7, 8]. Restricting further discussion to the first approach, its advantage is that it may combine the flexibility of the weaker interaction with the strength of coordination bonding. This route can be exemplified by considering the pyridyl amides where the pyridine nitrogen atom can bind to

a metal ion, with the neutral amide group forming self-complementary hydrogen-bonds to neighbouring ligands [9]. From a crystal engineering viewpoint, the advantage of using transition metals is that the shape of the main building unit can be controlled by using a metal-ligand system that is known to exhibit a desired coordination geometry [5]. A specific geometry can be propagated throughout the crystal structure by attaching substituents to the ligands; these substituents act as intermolecular connectors [5, 6].

We have recently [10–13] embarked on a programme which has as a short-term goal the creation of novel supramolecular architectures based on hydrogen-bonding interactions between *simple* metal complexes. This project can be regarded as an extension of our work in the field of coordination polymers [14–21]. Our long-term goal is to combine co-

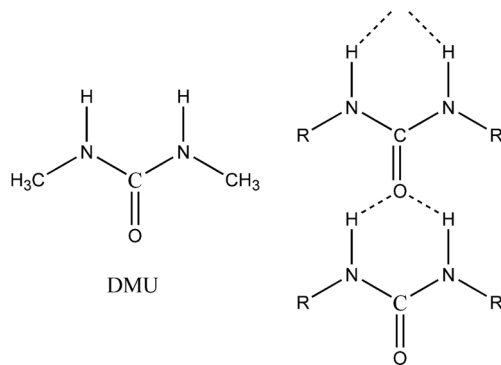


Fig. 1. The chemical formula of *N,N'*-dimethylurea (DMU) and a small part (which contains only two molecules) of the α -network commonly observed in symmetrically disubstituted ureas.

ordination polymers and ligand-based hydrogen-bonds to create novel supramolecular architectures. Strategies available for the achievement of this goal have been reviewed [5, 6].

Ureas have long been employed in organic crystal engineering [22–24]. In particular, symmetrically disubstituted ureas form α -networks with each urea molecule donating two hydrogen-bonds and “chelating” the carbonyl oxygen atom of the next molecule in the network (Fig. 1). In contrast to the great number of studies concerning free ureas [22–25], little is known about the supramolecular architectures based on hydrogen-bonding interactions between simple metal-urea complexes. We are currently interested in the networks formed by simple metal/*N,N'*-dimethylurea (MeHNCONHMe, hereafter abbreviated as DMU, Fig. 1) complexes. By reacting metal ions with DMU, a ligand that contains both an efficient coordination site (the carbonyl oxygen atom) and two hydrogen-bonding functionalities (the –NH– groups), assembly can be dictated by intermolecular hydrogen-bonding interactions. We reported that $[M(\text{DMU})_6]^{2+}$ cations ($M = \text{Mn, Co, Ni, Zn}$) and counter anions (ClO_4^- , BF_4^- , NO_3^-) self-assemble to form hydrogen-bonded 1D or 2D architectures [11, 12]. The employment of weakly coordinating anions resulted in infinite assemblies based exclusively on ligand-counter ion hydrogen-bonds, which are not, strictly speaking, ligand-based hydrogen-bonded assemblies. Since crystal engineering of hydrogen-bonded, metal-containing networks has focused mainly on 3d-metals, Pd(II), Pt(II) and Ag(I) [4–6], and since the role of metal ions in supramolecular systems is of great importance, we recently studied [13] reactions be-

tween lanthanides(III) and DMU. It was shown that the $[\text{Ln}(\text{DMU})_6]^{3+}$ cations ($\text{Ln} = \text{Pr, Nd, Gd, Er}$) can act as hydrogen-bonding building blocks with multi-fold connectivity linking anions $[\text{LnCl}_6]^{3-}$ to generate 3D architectures. It was also shown that the hydrogen-bonding functionalities on the $[\text{Ln}(\text{NO}_3)_3(\text{DMU})_3]$ molecules yield 3D assemblies without the intervention of anionic intermediates.

This paper describes the full structural and IR characterization of the products from the reactions between yttrium(III) chloride and nitrate with DMU. We used anions (Cl^- , NO_3^-) that normally coordinate to Y^{III} to avoid the structural interference induced by the chemical and steric demands of a counter anion. A main goal of our study was to compare the structures and spectroscopic characteristics of the yttrium(III) complexes to the analogous lanthanide(III) complexes.

Results and Discussion

Preliminary considerations

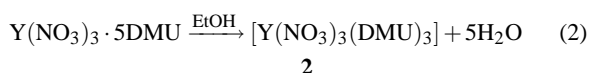
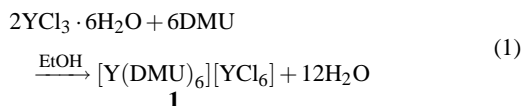
In the older literature in particular, it is not uncommon to find explicitly or implicitly that a Y complex of a given set of ligands will be isostructural with the corresponding late lanthanide(III) compounds. The reasoning for this is that Y has radii (atomic, metallic, ionic) that fall close to those of Er and Ho, and all of its chemistry is in the trivalent state [26]. The testing of this belief has been carried out for only a few species [27, 28]. Four years ago we decided to test the above viewpoint thoroughly at a more detailed level by preparing and characterizing Y(III) complexes of ligands with O- and/or N-donor groups, and by comparing their structures and chemistry with their Ln(III) analogues ($\text{Ln} = \text{lanthanide}$). At first we prepared and structurally characterized [29] complexes $[\text{Y}(\text{NO}_3)_3(\text{bpy})_2]$ and $[\text{Y}(\text{NO}_3)_3(\text{phen})_2]$ ($\text{bpy} = 2,2'$ -bipyridine; $\text{phen} = 1,10$ -phenanthroline) which were proved to be isostructural with their Ln(III) counterparts [30–32]. In a second project we reported [33] complexes $[\text{Y}(\text{NO}_3)_3(\text{terpy})(\text{H}_2\text{O})]$ and $[\text{Y}(\text{NO}_3)_3(\text{terpy})(\text{H}_2\text{O})] \cdot \text{terpy}$ ($\text{terpy} = 2,2':6',2''$ -terpyridine), which have their structural analogues in 4f metal/ NO_3^- /terpy chemistry; the former is isostructural with $[\text{Tm}(\text{NO}_3)_3(\text{terpy})(\text{H}_2\text{O})]$ [34], while the latter is isostructural with $[\text{Ln}(\text{NO}_3)_3(\text{terpy})(\text{H}_2\text{O})] \cdot \text{terpy}$ ($\text{Ln} = \text{Ho, Er}$) [34].

As part of our ongoing studies into the crystal engineering of hydrogen-bonded, metal-containing networks and the coordination chemistry of Y(III), we

were interested in the comparison of the *molecular* and *supramolecular* structures of the $\text{Y}^{\text{III}}/\text{X}^-/\text{DMU}$ ($\text{X}^- = \text{Cl}^-, \text{NO}_3^-$) complexes with those of the $\text{Ln}^{\text{III}}/\text{X}^-/\text{DMU}$ systems.

Brief synthetic comments

The preparation of the two complexes reported in this work is summarized in eqs (1) and (2):



Complexes **1** and **2** seem to be the only products from the $\text{YCl}_3 \cdot 6\text{H}_2\text{O}/\text{DMU}$ and $\text{Y}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}/\text{DMU}$ reaction systems in alcohols (EtOH, MeOH). The DMU:Y^{III} ratio and the crystallization method (addition of a precipitation solvent or slow evaporation at room temperature) both have no influence on the identity of the products. Thus, despite our efforts we could not obtain neutral chloro complexes, *i.e.* $[\text{YCl}_3(\text{DMU})_x]$ ($x = 3, 4, \dots$), or cationic complexes with nitrates as counterions, *i.e.* $[\text{Y}(\text{DMU})_x](\text{NO}_3)_3$ ($x = 6, 7, \dots$). It is also of interest that the two products have been crystallized from good donor solvents, such as alcohols, without the solvent participating in the coordination sphere of Y^{III} (indeed, alcohols have been employed as a useful means of occupying some metal ion coordination sites, so that any tendency toward formation of compounds with DMU:Y^{III} ratios less than 3 would have been enhanced).

Description of structures

Selected bond lengths and angles for complexes **1** and **2** are listed in Tables 1 and 2, respectively. Drawings of the complex ions of **1** are shown in Figs. 2 and 3. The molecular structure of **2** is depicted in Fig. 4, while the coordination polyhedron of the Y^{III} ion is shown in Fig. 5.

Complex **1** crystallizes in the hexagonal space group $R\bar{3}$. Its structure consists of almost perfect octahedral $[\text{Y}(\text{DMU})_6]^{3+}$ and $[\text{YCl}_6]^{3-}$ ions. The Y^{III} ions of the complex cation and anion sit on threefold axes of inversion. As a result there is only one crystallographically independent DMU ligand in the cation; the same

Table 1. Selected bond lengths (Å) and angles (°) relevant to the yttrium coordination spheres for complex **1**.

$[\text{Y}(\text{DMU})_6]^{3+}$		$[\text{YCl}_6]^{3-}$	
Y(2)-O(1)	2.209(2)	Y(1)-Cl(1)	2.623(1)
C(2)-O(1)	1.258(3)		
C(2)-N(1)	1.325(5)		
C(2)-N(2)	1.321(5)		
O(1)-Y(2)-O(1)	180, 90.8(1), 89.2(1)	Cl(1)-Y(1)-Cl(1)	180, 91.0(1), 89.0(1)
C(2)-O(1)-Y(2)	170.0(2)		

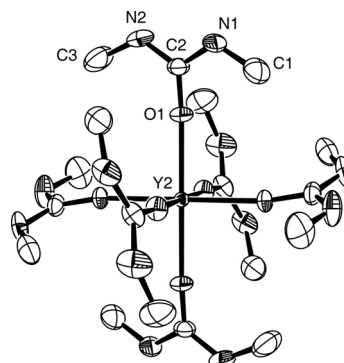


Fig. 2. The molecular structure of the cation $[\text{Y}(\text{DMU})_6]^{3+}$ present in the crystal structure of **1**. For clarity, only the atoms of one DMU ligand have been labelled.

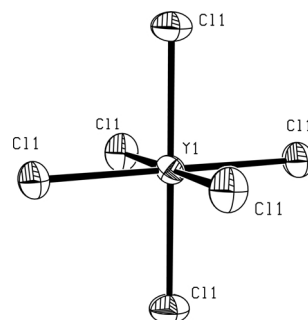
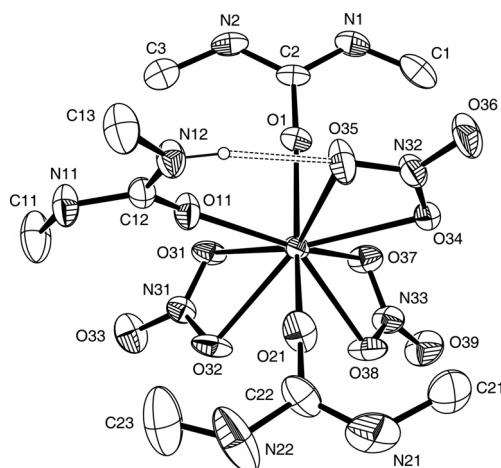


Fig. 3. The molecular structure of the anion $[\text{YCl}_6]^{3-}$ present in the crystal structure of **1**. An identical labeling scheme is used for the chloro atoms generated by symmetry.

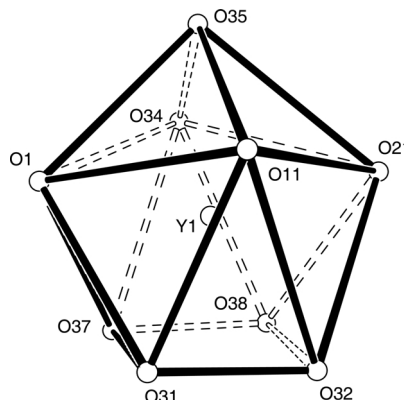
applies to the chloro ligands in $[\text{YCl}_6]^{3-}$. The Y-O distance [2.209(2) Å] is shorter than the Nd-O distance [2.313(3) Å] in the corresponding octahedral cation $[\text{Nd}(\text{DMU})_6]^{3+}$ [13]. Due to coordination, the C=O bond distance in **1** [1.258(3) Å] is slightly longer than the C=O bond length in free DMU [1.242 Å] [35]. The amide-type C(2)-N(1) and C(2)-N(2) bonds are short [average 1.323(5) Å], as expected for the amide resonance [36]. The Y-Cl bond length in **1** [2.623(1) Å] compares well with Y-Cl distances in other struc-

Table 2. Selected bond lengths (Å) and angles (°) relevant to the yttrium coordination sphere for complex **2**.

Y(1)-O(1)	2.211(7)	C(12)-N(12)	1.344(9)
Y(1)-O(11)	2.243(5)	C(22)-O(21)	1.254(12)
Y(1)-O(21)	2.249(6)	C(22)-N(21)	1.341(16)
Y(1)-O(31)	2.495(5)	C(22)-N(22)	1.323(13)
Y(1)-O(32)	2.485(5)	N(31)-O(31)	1.238(8)
Y(1)-O(34)	2.460(4)	N(31)-O(32)	1.247(8)
Y(1)-O(35)	2.474(5)	N(31)-O(33)	1.210(9)
Y(1)-O(37)	2.481(5)	N(32)-O(34)	1.265(7)
Y(1)-O(38)	2.424(5)	N(32)-O(35)	1.238(8)
C(2)-O(1)	1.287(10)	N(32)-O(36)	1.232(8)
C(2)-N(1)	1.302(12)	N(33)-O(37)	1.261(8)
C(2)-N(2)	1.340(13)	N(33)-O(38)	1.234(8)
C(12)-O(11)	1.258(9)	N(33)-O(39)	1.214(9)
C(12)-N(11)	1.309(9)		
O(1)-Y(1)-O(11)	85.2(3)	O(37)-Y(1)-O(38)	50.8(2)
O(1)-Y(1)-O(21)	153.8(3)	C(2)-O(1)-Y(1)	171.9(8)
O(1)-Y(1)-O(37)	74.8(3)	C(12)-O(11)-Y(1)	152.5(5)
O(11)-Y(1)-O(21)	82.3(2)	C(22)-O(21)-Y(1)	163.2(7)
O(11)-Y(1)-O(32)	77.6(2)	O(31)-N(31)-O(32)	114.7(6)
O(11)-Y(1)-O(38)	145.5(2)	O(31)-N(31)-O(33)	125.4(7)
O(21)-Y(1)-O(34)	85.0(2)	O(32)-N(31)-O(33)	119.9(7)
O(21)-Y(1)-O(37)	125.4(2)	O(34)-N(32)-O(35)	116.5(6)
O(21)-Y(1)-O(38)	75.2(2)	O(34)-N(32)-O(36)	121.2(6)
O(31)-Y(1)-O(32)	49.7(2)	O(35)-N(32)-O(36)	122.2(7)
O(31)-Y(1)-O(38)	95.3(2)	O(37)-N(33)-O(38)	115.1(6)
O(34)-Y(1)-O(35)	51.1(2)	O(37)-N(33)-O(39)	121.8(8)
O(34)-Y(1)-O(37)	75.6(2)	O(38)-N(33)-O(39)	123.0(8)

Fig. 4. The molecular structure of complex **2**. The double dashed line indicates the intramolecular hydrogen-bond; only the hydrogen atom H(N12) is shown.

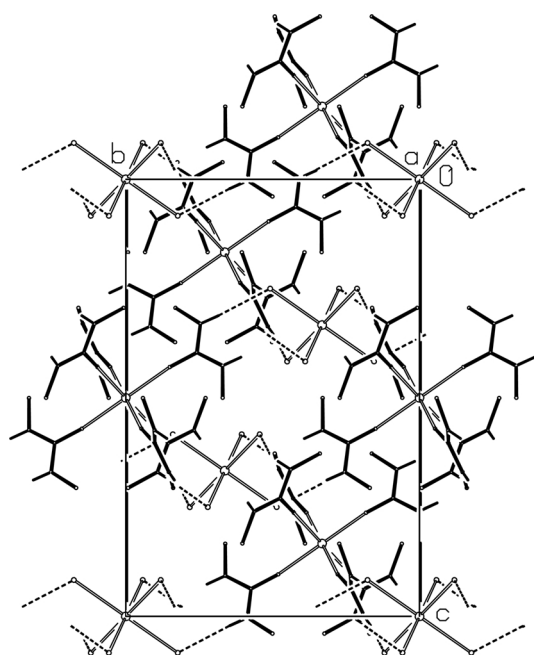
turally characterized six-coordinate yttrium(III) complexes containing terminal chloro ligands [37]. Compound **1** is the *second* structurally characterized yttrium(III) chloro complex containing the $[\text{YCl}_6]^{3-}$ anion. Reaction of RbCl with YCl_3 at 850–900 °C led to the isolation of $\text{Rb}_3[\text{YCl}_6]$; the structure of this salt has been determined [38].

Fig. 5. A view of the coordination polyhedron of **2** showing the distorted monocapped square antiprismatic coordination of the Y^{III} atom.

The molecular structure of **2** consists of mononuclear $[\text{Y}(\text{NO}_3)_3(\text{DMU})_3]$ molecules. The Y^{III} ion is in a nine-coordinate environment comprising six oxygen atoms from the three chelating nitrate groups and the oxygen atoms from the three monodentate DMU ligands. The coordinated nitrate groups are bound in the bidentate symmetrical mode, one of the several modes of coordination of this anion [39]. As has been recognized before [40], the coordinated nitrate O atoms (O_c) have longer N–O distances than the uncoordinated or “free” N–O, and the O_c –N– O_c angles $[114.7(6)–116.5(6)^\circ]$ are smaller than the idealized 120° value of the isolated NO_3^- anion. The average $\text{Y}(1)\text{--O}(\text{nitrate})$ distance in **2** (2.470 Å) is very similar to that found in other structurally characterized 9-coordinate $\text{Y}(\text{III})$ complexes containing bidentate chelating nitrate groups, for example in $[\text{Y}(\text{NO}_3)_3(\text{Ph}_3\text{PO})_2(\text{EtOH})]$ (2.39–2.47 Å) [40], $[\text{Y}(\text{NO}_3)_3(\text{Ph}_3\text{PO})_3]$ (2.40–2.51 Å) [40], $[\text{Y}(\text{NO}_3)_3\text{--}(\text{Ph}_2\text{MePO})_3]$ (2.41–2.49 Å) [40], $[\text{Y}(\text{NO}_3)_3\text{--}(\text{Me}_3\text{PO})_3]$ (2.44–2.53 Å) [40], $[\text{Y}(\text{NO}_3)_3(\text{H}_2\text{O})_3] \cdot \text{DB24C8}$ (2.43 Å) [41] and $[\text{Y}(\text{NO}_3)_3(\text{H}_2\text{O})_2(\text{MeCN})] \cdot [\text{Y}(\text{NO}_3)_3(\text{H}_2\text{O})_2(\text{MeOH})] \cdot \text{B15C5} \cdot \text{MeOH}$ (2.42 Å) [42], where DB24C8 is dibenzo-24-crown-8 and B15C5 is benzo-15-crown-5. If each NO_3^- ligand is conceptually [40, 43] considered as monoatomic (with the bonds directed towards the centers of the bidentate nitrate groups instead of towards the oxygen atoms), then the molecule can be described as distorted *mer*-(pseudo)octahedral. In accordance with an octahedral description of **2**: (i) The $\text{Y}(1)\text{--N}(31,32,33)$ distances $[2.883(7)–2.919(6) \text{ Å}]$ could be regarded as weakly bonding, and (ii) the $\text{O}(1)\text{--Y}(1)\text{--O}(11)$, $\text{O}(1)\text{--}$

Table 3. Dimensions of the crystallographically unique hydrogen-bonds (distances in Å and angles in °) for complexes **1** and **2**.

H bond	D...A	H...A	D-H...A	Operator of A
Complex 1 :				
N(2)-H(N2)...Cl(1)	3.270	2.455	176.5	$\frac{1}{3} - x, \frac{1}{3} - x, -\frac{1}{3} - z$
Complex 2 :				
N(12)-H(N12)...O(35) ^a	3.071	2.312	147.4	x, y, z
N(12)-H(N12)...O(33)	3.076	2.43	132.3	$-\frac{1}{2} + x, \frac{1}{2} + y, z$
N(1)-H(N1)...O(38)	3.051	2.356	139.0	$-\frac{1}{2} + x, \frac{1}{2} + y, z$
N(2)-H(N2)...O(32)	2.962	2.153	156.6	$-\frac{1}{2} + x, \frac{1}{2} + y, z$
N(11)-H(N11)...O(36)	3.166	2.381	152.0	$x, -y, -\frac{1}{2} + z$
N(21)-H(N21)...O(31)	2.966	2.351	128.8	$x, -1 + y, z$

^a Intramolecular hydrogen-bond; A = acceptor; D = donor.Fig. 6. A view (down *a*) of the 3D network of complex **1**.

Y(1)-O(21), O(11)-Y(1)-O(21), O(1)-Y(1)-N(32), N(31)-Y(1)-N(33) and N(32)-Y(1)-N(33) angles are 85.2(3), 153.8(3), 82.3(2), 174.8(2), 85.9(2), and 99.2(2)°, respectively, fairly close to the idealized octahedral values (90, 180°). The Y(1)-O(DMU) distances are ~0.25 Å shorter than the Y-O(nitrate) ones. If each NO₃⁻ is considered as a normal bidentate ligand, then the coordination polyhedron of Y(1) comes closer to a distorted monocapped square antiprism [44] with the nitrate oxygen O(35) forming the cap of the “square” O(1)O(11)O(21)O(34) base (Fig. 5). The small bite angle of the nitrate ligands is primarily responsible for the distortion of the coordination polyhedron. There is one intramolecular hydrogen-bond

of moderate strength with atom N(12) as donor and coordinated nitrate atom O(35) as acceptor (Fig. 4, Table 3). Complex **2** joins a relatively small family of yttrium(III) nitrate complexes [29, 33, 40–42, 45].

The DMU ligands in **1** and **2** are coordinated in a rather linear fashion, with Y-O-C angles ranging from 152.5(5) to 171.9(8)°. Linearly or approximately linearly coordinated urea or urea derivatives are extremely unusual and have been observed only in few cases [13, 46, 47]. The bent mode is the usual way of coordination of ureas [11, 12, 46].

Complexes **1** and **2** extend to fifteen the number of structurally characterized metal complexes of DMU. The thirteen, previously structurally characterized examples are [Mn(NO₃)₂(DMU)₃] [48], [MnBr₂(DMU)₃] [47], [Fe(DMU)₆](ClO₄)₃ [49], [Er(DMU)₆(H₂O)](ClO₄)₃ [50], [Co(DMU)₆]X₂ (X = ClO₄, BF₄, NO₃) [12], [M(DMU)₆](ClO₄)₂ (M = Mn, Ni, Zn) [11], [Cu(OCIO₃)(DMU)₄] [11], [Nd(DMU)₆][NdCl₆] [13], and [Nd(NO₃)₃-(DMU)₃] [13].

We have up to now discussed aspects of the molecular structures of complexes **1** and **2**. Figs. 6 and 7 provide views of the hydrogen-bonded networks of the two complexes. Distances and angles for the hydrogen-bonds present in the crystal structures are listed in Table 3.

There is one crystallographically unique, interionic hydrogen-bond in **2**. However, due to the high symmetry, the [Y(DMU)₆]³⁺ cations and [YCl₆]³⁻ anions self-assemble to form a 3D hydrogen-bonded architecture. All chloro ligands from [YCl₆]³⁻ act as hydrogen-bond acceptors to NH groups from DMU ligands. Six out of twelve NH groups, each belonging to a different DMU molecule, participate in hydrogen-bonds. Each [Y(DMU)₆]³⁺ cation is connected with six [YCl₆]³⁻ anions and, conversely, each [YCl₆]³⁻ anion is hydrogen-bonded to six [Y(DMU)₆]³⁺ cations. Hydrogen-bonds with halogen acceptors are of current interest [51, 52]; a metal-bound halogen is strongly polar and a good acceptor. In addition, there is one crystallographically unique weak hydrogen-bonding interaction (not included in Table 3 and not shown in Fig. 6) with one methyl carbon as donor and the coordinated chloro ligand as acceptor. The dimensions of this interaction are: C(3)...Cl(1) 3.816 Å, H(3B)...Cl(1) 2.778 Å, C(3)-H(3B)...Cl(1) 164.6°. Under this scheme, each [Y(DMU)₆]³⁺ cation interacts with two [YCl₆]³⁻ an-

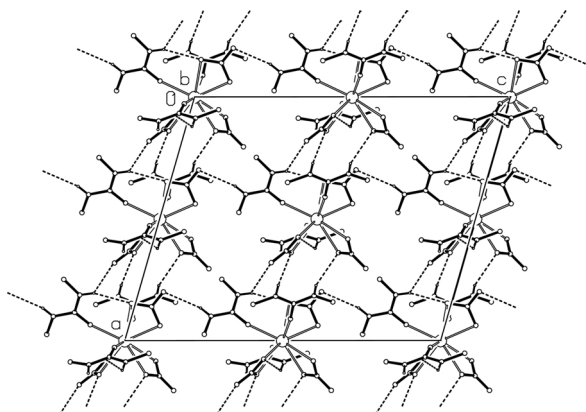


Fig. 7. A view (down *b*) of the 3D network of complex **2**.

ions. Formerly considered “unusual” or “nonconventional”, weak hydrogen-bonds with C-H groups as donors are now discussed frequently in many fields of structural chemistry [22, 23, 51] and biology [53, 54].

The $[\text{Y}(\text{NO}_3)_3(\text{DMU})_3]$ molecules in **2** are arranged in infinite 3D networks through five intermolecular N-H \cdots O(nitrato) hydrogen-bonds. Five, out of the six available, NH groups participate in hydrogen-bonds. One nitrato ligand accepts hydrogen-bonds through all its oxygen atoms [O(31), O(32), O(33)], another through two of its oxygen atoms [O(35), O(36)] and the remaining nitrato ligand accepts hydrogen-bonds only through its coordinated atom O(38). It is worth noting that the N(12)-H(N12) group forms a bifurcated hydrogen-bond, the acceptor atoms being O(35) [*x*, *y*, *z*] and O(33) [$-1/2 + x$, $1/2 + y$, *z*]. The N(1)-H(N1) \cdots O(38), N(2)-H(N2) \cdots O(32) and N(21)-H(N21) \cdots O(31) hydrogen-bonds are responsible for the formation of layers parallel to the *ab* plane. The N(11)-H(11) \cdots O(36) hydrogen-bonds link the layers together resulting in the formation of the 3D network.

Most hydrogen-bonds in the supramolecular structures of **1** and **2** can be characterized as “moderate” [51].

Infrared characterization

The full vibrational analysis of crystalline free, *i. e.*, uncoordinated DMU, has been published [55]. Table 4 gives diagnostic IR bands of the free ligand, and its yttrium(III) complexes **1** and **2**. Assignments in Table 4 have been given in comparison with the data obtained for the free ligand [55], for its 3d- [11, 12, 48] and 4f-metal [13] complexes, and by studying the new bands in **2** (due to nitrate vibrations).

Table 4. Most characteristic and diagnostic IR data (cm^{-1}) of free DMU^a and its yttrium(III) complexes **1** and **2**.

DMU	1	2	Assignments
~ 3350 sb	3358 sb	3358 s, 3325 s	$\nu(\text{NH})$
1628 s	1612 sb	1616 sb	$\nu(\text{CO})$
		1674 m	$\nu_1(\text{A}_1)\text{NO}_3^-^b$
1591 s	1630 sh	1637 sh	$\delta_{\text{as}}(\text{NH})$
1541 m	1514 w	1510 m	$\delta_{\text{s}}(\text{NH})$
1270 sb	1310 m		$\nu_{\text{as}}(\text{CN})_{\text{amide}}^c$
		1304 s	$\nu_{\text{as}}(\text{CN})_{\text{amide}}, \nu_5(\text{B}_2)\text{NO}_3^-^b$
1175 m	1178 m	1178 m	$\nu_{\text{s}}(\text{N-CH}_3)$
1040 m	1048 m		$\nu_{\text{as}}(\text{N-CH}_3)$
		1040 m	$\nu_{\text{as}}(\text{N-CH}_3), \nu_2(\text{A}_1)\text{NO}_3^-^b$
931 m	939 w	938 w	$\nu_{\text{s}}(\text{CN})_{\text{amide}}^c$
775 m	762 m		$\pi(\text{CO})$
		754 m	$\pi(\text{CO}), \nu_3(\text{A}_1)\text{NO}_3^-^b$
702 w	667 sh	696 sh	$\delta(\text{CO})$
576 mb	648 mb	628 mb	$\pi_{\text{as}}(\text{NH})$

^a In its *Cc* crystal phase; ^b the cited wavenumbers of the nitrato ligands arise from spectra recorded as Nujol and hexachlorobutadiene mulls (see text); ^c these modes refer to the $-\text{NH-CO-NH}-$ group; b = broad; m = medium; s = strong; sh = shoulder; w = weak.

The bands with $\nu_{\text{as}}(\text{CN})_{\text{amide}}$ character are situated at higher frequencies in the spectra of **1** and **2** than for free DMU, whereas the $\nu(\text{CO})$ band shows a frequency decrease. These shifts are consistent with oxygen coordination, suggesting the presence of $^+\text{N}=\text{C}-\text{O}^-$ resonant forms [11, 12, 47, 48]. Upon coordination *via* oxygen, the positively charged Y^{III} ion stabilizes the negative charge on the oxygen atom; the NCO group now occurs in its polar resonance form and the double bond character of the CN bond increases resulting in an increase of the CN stretching frequency, while the double bond character of the CO bond decreases resulting in a decrease in the CO stretching frequency.

The nitrate frequencies for **2** cited in Table 4 arise from spectra recorded as mulls (Nujol, hexachlorobutadiene), since it is well established that pressing a KBr pellet affects the nitrate coordination [56]; as expected, the ligand's or **1** wavenumbers are identical in both KBr and mull spectra. The nitrate vibrations in the mull spectra of **2** are indicative of the presence of bidentate nitrato groups, because [57] the separation of the two highest-wavenumber bands $\nu_1(\text{A}_1)$ and $\nu_5(\text{B}_2)$ [under C_{2v} symmetry] is large ($\sim 370 \text{ cm}^{-1}$). The IR spectrum of this complex in KBr is complicated indicating the simultaneous presence of coordinated and ionic nitrates; the existence of the latter is deduced from the appearance of the $\nu_3(\text{E}')[\nu_{\text{d}}(\text{NO})]$ mode of the D_{3h} ionic nitrate at $\sim 1385 \text{ cm}^{-1}$, suggesting that a certain amount of nitrato ligands are replaced by bromides in the KBr matrix (thus generating ionic nitrates) [56].

Concluding Comments and Perspectives

Complexes **1** and **2** are interesting hydrogen-bonded networks based on simple complex ions (**1**) or molecules (**2**). Research in progress reveals that the hexakis-(N,N'-dimethylurea)yttrium(III) cation can act as a hydrogen-bonding building block linking several inorganic or organic anions and generating a rich diversity of networks. We also work on other neutral yttrium(III) complexes of DMU using pseudohalides (SCN^- , SeCN^- , ...) as coligands to take advantage of the fact that those ligands have a poor hydrogen-bonding ability, thus favouring $\text{DMU} \cdots \text{DMU}$ hydrogen-bonded yttrium(III) assemblies.

The N-H hydrogen atoms of symmetrically disubstituted ureas, like DMU, prefer to adopt an *anti,anti* (or *trans,trans* [55]) relationship to the carbonyl group and to form three-center bonds to urea carbonyl groups [23,24], see Fig. 1. Coordination of DMU to Y^{III} has the following consequences. First, the electron pair available on the carbonyl oxygen atom of DMU does not act as a hydrogen-bond acceptor in **1** and **2**. The inability of the carbonyl DMU oxygen atom to participate in a hydrogen-bond was also observed in complexes $[\text{Nd}(\text{DMU})_6][\text{NdCl}_6]$ and $[\text{Nd}(\text{NO}_3)_3(\text{DMU})_3]$ [13], by contrast with the 3d-metal complexes of DMU [11,12]. Second, the N-H hydrogen atoms of each coordinated DMU in **1** adopt an *anti,anti* (or *trans,trans*) relationship to the carbonyl group (like in free DMU [35,55]) to participate in interionic hydrogen-bonds with the chloro ligands of $[\text{YCl}_6]^{3-}$. However, contrary to the situation in $[\text{Nd}(\text{DMU})_6][\text{NdCl}_6]$ where ten out of twelve NH groups participate in hydrogen-bonds [13], only half (*i.e.*, six) of the twelve available NH groups hydrogen-bond to chloro ligands. The N-H hydrogen atoms of two coordinated DMU ligands in **2** [those containing atoms N(1), N(2) and N(21), N(22)] also adopt an *anti,anti* (or *trans,trans*) relationship to the carbonyl group (like in free DMU), three of them participating in intermolecular hydrogen-bonds with nitrate oxygen atoms. However, contrary to the situation in $[\text{Nd}(\text{NO}_3)_3(\text{DMU})_3]$ [13] where all three DMU ligands have their N-H hydrogen atoms in *anti,anti* (or *trans,trans*) relationships to their respective carbonyl groups, the N-H hydrogen atoms of the third coordinated DMU ligand in **2** [that containing atoms N(11), N(12)] adopt the *syn,anti* (or *cis,trans*)

relationship to its coordinated carbonyl group. The *syn* (or *cis*) configuration of the N(12)H(N12) group is necessary for the formation of the unique (see Table 3) intramolecular hydrogen-bond; this hydrogen-bond creates a six-membered pseudochelating $\text{Y}(1)\text{O}(11)\text{C}(12)\text{N}(12)\text{H}(\text{N}12) \cdots \text{O}(35)$ ring, providing an extra stabilization to the $[\text{Y}(\text{NO}_3)_3(\text{DMU})_3]$ molecule. It is worth noting that there is no such intramolecular hydrogen-bond in $[\text{Nd}(\text{NO}_3)_3(\text{DMU})_3]$ [13].

The role of metal ions in supramolecular systems may simply be to act as coordination centers providing a template for the formation of a rigid framework of remote hydrogen-bonding sites [4]. Alternatively, the metal ion may exert an electronic effect on the individual proton donor and acceptor sites, and influence hydrogen-bonding in a more subtle manner [4]. We do believe that the latter effect is responsible for the differences observed between the supramolecular structures of **1**, **2** and their lanthanide(III) counterparts [13].

Experimental Section

All manipulations were performed under aerobic conditions using materials and solvents (Merck, Aldrich) as received. Elemental analyses (C, H, N) were conducted by the University of Ioannina, Greece, Microanalytical Service using an EA 1108 Carlo Erba analyzer. IR spectra ($4000 - 500 \text{ cm}^{-1}$) were recorded on a Perkin-Elmer 16PC FT spectrometer with samples prepared as KBr pellets. IR spectra of the nitrate compound **2** were also recorded and averaged on a Bruker IFS 113v FT spectrometer, using a liquid nitrogen-cooled MCT detector, with samples prepared as Nujol or hexachlorobutadiene mulls between CsI discs.

$[\text{Y}(\text{DMU})_6][\text{YCl}_6]$ (**1**)

A colourless solution of $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ (0.41 g, 1.4 mmol) in EtOH (20 ml) was treated with solid DMU (0.44 g, 5.0 mmol). DMU soon dissolved to give a homogeneous solution, which was stirred for 5 min. The solution was layered with *n*-hexane (30 ml). Slow mixing gave well-formed, X-ray quality colourless prismatic crystals, which were collected by filtration, washed with Et_2O (3 ml) and dried *in vacuo* over silica gel. Typical yield (based on $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$) were in the 55–65% range. $-\text{C}_{18}\text{H}_{48}\text{N}_{12}\text{O}_6\text{Cl}_6\text{Y}_2$ (919.20): calcd. C 23.52, H 5.27, N 18.29; found C 23.70, H 5.13, N 17.99.

Table 5. Summary of crystal data, data collection and structure refinement for the X-ray diffraction study of complexes **1** and **2**.

Complex	1	2
Chemical formula	C ₁₈ H ₄₈ N ₁₂ O ₆ Cl ₆ Y ₂	C ₉ H ₂₄ N ₉ O ₁₂ Y
Formula weight	919.20	538.28
Colour, habit	colourless prisms	colourless prisms
Crystal system	hexagonal	monoclinic
Space group	$R\bar{3}$	Cc
<i>a</i> [Å]	13.871(6)	14.859(8)
<i>b</i> [Å]	13.871(6)	8.814(4)
<i>c</i> [Å]	13.846(9)	18.530(8)
β [°]	90	106.03(2)
<i>V</i> [Å ³]	2974(2)	2332.4(2)
<i>Z</i>	3	4
<i>D</i> _{calc} [g cm ⁻³]	1.540	1.536
μ [mm ⁻¹]	3.363	2.570
<i>F</i> (000)	1404	1104
Radiation [Å]	Mo- <i>K</i> α	Mo- <i>K</i> α
	($\lambda = 0.71073$)	($\lambda = 0.71073$)
Temperature [K]	298	298
Scan mode/speed [° min ⁻¹]	$\theta - 2\theta/3.6$	$\theta - 2\theta/2.0$
θ Range [°]	2.04–24.99	2.29–24.01
Ranges <i>h</i>	–13 → 14,	–16 → 16,
<i>k</i>	–13 → 14,	–10 → 0,
<i>l</i>	–21 → 21	–21 → 21
Measured reflections	2336	3639
Unique reflections	1168	3639
	(<i>R</i> _{int} = 0.0428)	<i>R</i> _{int} = 0.0000)
Reflections used		
[<i>I</i> > 2 σ (<i>I</i>)]	975	2968
Parameters refined	100	298
<i>w</i> ^a	<i>a</i> = 0.0399; <i>b</i> = 1.2026	<i>a</i> = 0.0395; <i>b</i> = 3.6792
GoF (on <i>F</i> ²)	1.031	1.039
<i>R</i> 1 ^b [<i>I</i> > 2 σ (<i>I</i>)]	0.0291	0.0447
<i>wR</i> 2 ^c [<i>I</i> > 2 σ (<i>I</i>)]	0.0719	0.1015
($\Delta\rho$) _{max} /($\Delta\rho$) _{min} (e Å ⁻³)	0.266/–0.527	0.420/–0.425

^a $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = (\max(F_o^2, 0) + 2F_c^2)/3$; ^b $R1 = \sum(|F_o| - |F_c|)/\sum(|F_o|)$; ^c $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

[Y(NO₃)₃(DMU)₃] (**2**)

A colourless solution of Y(NO₃)₃ · 5H₂O (0.29 g, 0.8 mmol) in EtOH (20 ml) was added to a colourless solu-

tion of DMU (0.35 g, 4.0 mmol) in the same solvent (20 ml). No noticeable colour appeared. The resulting solution was layered with a 1 : 1 mixture of *n*-hexane and Et₂O (total volume: 70 ml). Slow mixing yielded colourless, X-ray quality crystals of the product, which were collected by filtration, washed with cold EtOH (2 ml) and Et₂O (2 × 5 ml), and dried in air. The yield (based on Y^{III}) was ~70%. – C₉H₂₄N₉O₁₂Y (539.28): calcd. C 20.04, H 4.49, N 23.28; found C 19.71, H 4.59, N 21.11.

Crystal structure determinations

Colourless prismatic crystals of **1** (0.10 × 0.10 × 0.50 mm) and **2** (0.10 × 0.15 × 0.40 mm) were mounted in air. Diffraction measurements were made on a Crystal Logic Dual Goniometer diffractometer using graphite monochromated Mo radiation. Crystal data and full details of the data collection and data processing are listed in Table 5. Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections, in the range 11 < 2 θ < 23°. Three standard reflections, monitored every 97 reflections, showed less than 3% intensity variation and no decay. Lorentz, polarization and ψ scan (only for **2**) absorption corrections were applied using Crystal Logic Software.

The structures were solved by direct methods using SHELXS-86 [58] and refined by full-matrix least-squares techniques on *F*² with SHELXL-97 [59]. For both structures, all H atoms were located by difference maps and refined isotropically. All non-H atoms were refined using anisotropic displacement parameters. Two X-ray crystallographic files for complexes **1** and **2** in CIF format have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, under the numbers 258612 (**1**) and 258613 (**2**). Copies may be requested free of charge from the Director of CCDC (E-mail: deposit@ccdc.cam.ac.uk).

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