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Hydrogen bonded networks based on lanthanide(III) complexes of N,N'-dimethylurea (DMU): preparation, characterisation, and crystal structures of $[Nd(DMU)_6][NdCl_6]$ and $[Nd(NO_3)_3(DMU)_3]$

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Abstract

In order to examine the possibilities of using lanthanide(III) ions in the crystal engineering of hydrogen bonded coordination complexes, the compounds $[Ln(DMU)_6][LnCl_6]$ and $[Ln(NO_3)_3(DMU)_3]$ (Ln = Pr, Nd, Gd, Er; DMU = N,N'-dimethylurea) have been prepared from the reactions of DMU with the appropriate lanthanide(III) salts in alcohols. The representative complexes $[Nd(DMU)_6][NdCl_6]$ (**2**) and $[Nd(NO_3)_3(DMU)_3]$ (**6**) have been structurally characterised by single-crystal X-ray studies. The structure of **2** consists of distorted octahedral $[Nd(DMU)_6]^{3+}$ and $[NdCl_6]^{3-}$ ions. In the molecules of **6**, the Nd(III) ion is in a nine-coordinate, monocapped square antiprismatic geometry, surrounded by three O-bonded DMU ligands and three bidentate chelating nitrate groups. The $[Nd(DMU)_6]^{3+}$ cations and $[NdCl_6]^{3-}$ anions self-assemble to form a hydrogen-bonded 3D architecture in **2**. The hydrogen bonding functionalities on the molecules of **6** create also a 3D structure. Two main motifs of interionic/intermolecular hydrogen bonds have been observed: N–H···Cl in **2** and N–H···O(NO_3^-) in **6**; weak C–H···Cl hydrogen bonding interactions are also present in **2**. The complexes were characterised by magnetic susceptibilities at room temperature and spectroscopic (IR, far-IR, Raman) techniques. The vibrational data are discussed in terms of the nature of bonding and the known structures of the neodymium(III) complexes.

Keywords: Hydrogen bonded coordination complexes; Lanthanide(III) complexes; N,N'-dimethylurea metal complexes; Spectroscopic characterisation; X-ray crystal structures

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1. Introduction

At an early age, children are fascinated with building blocks and LEGOs because elaborate structures may be created from far simpler objects [1]. It is with the same enthusiasm and fascination that chemists have approached the idea of employing molecular building blocks to assemble noncovalent structures. The predictable and controlled assembly of molecules and ions in the solid state is one of the primary goals of crystal engineering, and the last dozen of years has seen the arrival of several useful tools for synthesising supramolecular assemblies [2–6]. The hydrogen bond is arguably the best intermolecular connector and hydrogen bonded motifs, such as carboxylic acid dimers and amide–amide ribbons, have been utilised in the design of extended assemblies in organic molecular solids [3,7–11].

More recently, intermolecular assembly of metal complexes via hydrogen bonding has gained attention, where, rather than forming the more common coordination polymers using coordination bonds [12–18], neighbouring metal complexes are connected and orientated through ligand–ligand or ligand–counter ion hydrogen bonds [19–30].

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From a crystal engineering standpoint, 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 [21]. A specific geometry can then be propagated throughout the crystal structure by attaching substituents to the ligands; these substituents act as intermolecular connectors. For example, Mingos and co-workers have used molecular recognition strategies to connect transition metal complexes as well as to link metal complexes to organic molecules using complementary hydrogen bonding groups [19]. Another example is the work of Aakeroy and Beatty who employed nicotinamide in the assembly of silver(I) complexes, where the pyridine nitrogen atom provides a coordinate interaction with the Ag(I) ion; the geometry encoded in these linear complexes was then propagated in a predictable manner via amide–amide hydrogen bonds between neighbouring cations [21].

We have recently [31,32] embarked on a programme which has as a short-term goal the creation of novel supramolecular structures based on hydrogen bonding interactions between simple metal complexes. This project can be regarded as an extension of our work in the area of coordination polymers [33–36]. Our long-term goal is to combine coordination polymers and ligand-based hydrogen bonds to create novel supramolecular architectures. Such an approach has some advantages, as it combines the strength of the coordination network and the flexibility imparted by the soft hydrogen bond interactions [37]. Available strategies for the achievement of this goal have been recently reviewed [20].

Ureas have been among the central players in organic crystal engineering [1,3,7,38,39]. In particular, symmetrical disubstituted ureas form α-networks with each urea molecule donating two hydrogen bonds and ‘chelating’ the carbonyl oxygen of the next molecule in the network (Fig. 1). In contrast to the great number of studies concerning free ureas [1,3,7,38–40], practically nothing is known about the supramolecular architectures based on hydrogen bonding interactions between simple metal–ureas complexes. We currently study the supramolecular structures of simple metal/*N*,*N*′-dimethylurea (MeHNCONHMe, hereafter abbreviated as DMU) complexes where, in principle, the oxygen atom of DMU can coordinate to the metal ion and/or provide a hydrogen bonding acceptor site. By reacting metal ions with a ligand, such as DMU, that contains both an efficient coordination site and two hydrogen bonding functionalities, assembly can be dictated by intermolecular hydrogen bonding interactions. In very recent papers [31,32], we described the preparation and crystal structures of complexes $[M(DMU)_6](ClO_4)_2$ [M = Mn, Co, Ni, Zn] and $[Co(DMU)_6]X_2$ (X = BF_4, NO_3). The $[M(DMU)_6]^{2+}$ and counter ions self-assemble to form hydrogen bonded 1D or 2D architectures. 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 to date focused mainly on first-row transition metals, Pd(II), Pt(II), Ag(I) and Cd(II), and since the role of metal ions in supramolecular systems is of great importance, we decided to study the reactions between lanthanides(III) and DMU, to see how incorporation of 4f metal ions might affect the molecular and supramolecular structures of the products. The present paper describes the preparation, structural characterisation and physical/spectroscopic study of the products from the reactions between selected lanthanide(III) chlorides and nitrates with DMU. We used anions (Cl^-, NO_3^-) that normally coordinate to lanthanides(III) to avoid the structural interference induced by the chemical and steric demands of a counter ion.

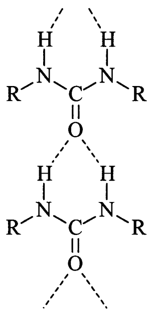

Fig. 1. A small part (which contains only two molecules) of the α-network commonly observed in symmetrical disubstituted ureas.

The present work can be also regarded as a continuation of our research in the spectroscopy of free ureas [40,41] and in the study of their coordination chemistry [42–44].

2. Experimental

2.1. General and physical measurements

All manipulations were performed under aerobic conditions using materials (reagent grade) and solvents as received.

Microanalyses (C, H, N) were performed by the University of Ioannina (Greece) Microanalytical Laboratory using an EA 1108 Carlo Erba analyser. The metal content was determined volumetrically with ethylenediaminetetra-acetate using Xylenol Orange as indicator. IR spectra (4000–500 cm^{-1}) were recorded on a Perkin–Elmer 16 PC FT spectrometer with samples prepared as KBr pellets and as Nujol or hexachlorobutadiene mulls between CsI discs. Far-IR spectra (500–50 cm^{-1}) were recorded on a Bruker IFS 113v FT spectrometer using polyethylene pellets. FT Raman data have been collected on a Bruker IFS 66v interferometer with a FRA 106 Raman module, a CW Nd: YAG laser source and a liquid nitrogen-cooled Ge detector. Magnetic susceptibilities were measured at room temperature (r.t.) using the Faraday method with a Cahn–Ventron RM-2 balance standardised with $HgCo(NCS)_4$; diamagnetic corrections were estimated from Pascal's constants.

2.2. Compound preparation

The lanthanide(III) chloride complexes were all prepared similarly; the same route was also used to prepare the nitrato complexes. Typical preparations for the representative complexes $[Nd(DMU)_6][NdCl_6]$ (**2**) and $[Nd(NO_3)_3(DMU)_3]$ (**6**) are given below. Colours, yields, analytical results and effective magnetic moment (μ_{eff}) values for the prepared complexes are given in Table 1.

2.2.1. $[Nd(DMU)_6][NdCl_6]$ (**2**)

A lilac solution of $NdCl_3 \cdot 6H_2O$ (0.18 g, 0.5 mmol) in EtOH (20 ml) was added to a colourless solution of DMU (0.22 g, 2.5 mmol) in the same solvent (20 ml). The resulting pale mauve solution was layered with *n*-hexane (50 ml). Slow mixing yielded lilac crystals (some of them were of X-ray quality), which were collected by filtration, washed with Et_2O and dried in air. Yield: 72%.

2.2.2. $[Nd(NO_3)_3(DMU)_3]$ (**6**)

A pale mauve solution of $Nd(NO_3)_3 \cdot 6H_2O$ (0.22 g, 0.5 mmol) in EtOH (15 ml) was added to a colourless solution of DMU (0.22 g, 2.5 mmol) in the same solvent. The resulting lilac solution was layered with a 1:1 mixture of *n*-hexane and Et_2O (40 ml). Slow mixing yielded pale mauve, X-ray quality crystals of the product, which were collected by filtration, washed with cold EtOH (2–3 ml) and Et_2O, and dried in air. Yield: 60%.

2.3. X-ray crystallographic studies

Crystals of complexes **2** and **6** were mounted in air. Diffraction measurements were made on a Crystal Logic Dual goniometer diffractometer using graphite-monochromated Mo radiation. Complete crystal data and parameters for data collection and processing are reported in Table 2. Unit cell dimensions were determined and refined using the angular settings of 25 automatically centred reflections in the range $11° < 2\theta < 23°$. Three standard reflections, monitored every 97 reflections, showed less than 3% fluctuation and no decay. Lorentz polarisation and Ψ-scan absorption corrections were applied using CRYSTAL LOGIC software.

The structures were solved by direct methods using SHELXS-86 [45] and refined by full-matrix least-squares techniques on F^2 with SHELXL-97 [46]. For **1** and **2**, all hydrogen atoms—except those on C(3) in **1**, and on C(1) and C(3) in **2** which were introduced at calculated positions as riding on bonded atoms—were clearly visible in subsequent difference Fourier maps and refined with anisotropic thermal parameters. For both structures, all non-hydrogen atoms were refined using anisotropic thermal parameters. In **6**, one of the DMU molecules was found disordered above and below the mirror plane passing through atoms Nd, O(1), O(2), O(3), N(5), O(5), N(6), O(7) and N(7). Thus, the atoms of the disordered DMU molecule were refined with occupation factors fixed to 10.5; as a result of the disorder, only two hydrogen atoms were found for each of the methyl carbon atoms [C(4) and C(6), see Fig. 4] of the disordered DMU ligand.

Table 1
Colours, yields, analytical results(%) [a] and effective magnetic moments for the new praseodymium(III), neodymium(III), gadolinium(III) and erbium(III) complexes of DMU

Number	Compound	Colour	Yield (%) [b]	M	C	H	N	μ_{eff} [c,d] (B.M.)
1	$[Pr(DMU)_6][PrCl_6]$	pale green	74	27.0 (27.5)	21.0 (21.1)	4.7 (4.7)	16.2 (16.4)	3.43
2	$[Nd(DMU)_6][NdCl_6]$	lilac	72	28.8 (28.0)	20.8 (21.0)	4.6 (4.7)	16.1 (16.3)	3.50
3	$[Gd(DMU)_6][GdCl_6]$	colourless	78	30.7 (29.8)	20.7 (20.5)	4.7 (4.6)	16.0 (15.9)	7.97
4	$[Er(DMU)_6][ErCl_6]$	pink	81	31.8 (31.1)	20.2 (20.1)	4.7 (4.5)	15.3 (15.6)	9.57
5	$[Pr(NO_3)_3(DMU)_3]$	pale green	57	24.6 (23.8)	18.4 (18.3)	4.2 (4.1)	21.3 (21.3)	3.47
6	$[Nd(NO_3)_3(DMU)_3]$	pale mauve	60	24.7 (24.3)	18.2 (18.2)	4.3 (4.1)	21.1 (21.2)	3.54
7	$[Gd(NO_3)_3(DMU)_3]$	cream	63	26.4 (25.9)	17.9 (17.8)	4.1 (4.0)	20.7 (20.8)	8.01
8	$[Er(NO_3)_3(DMU)_3]$	pink	69	26.4 (27.1)	17.6 (17.5)	3.9 (3.9)	20.2 (20.4)	9.51

M, metal.

[a] Calculated values in parentheses.

[b] Based on the metal.

[c] Per metal ion.

[d] At room temperature.

Table 2
Crystallographic data for complexes **2** and **6**

Parameter	**2**	**6**
Formula	$C_{18}H_{48}Cl_6N_{12}$-O_6Nd_2	$C_9H_{24}N_9O_{12}Nd$
Formula weight	1029.86	594.61
Crystal colour, habit	pale lilac, prism	pale lilac, prism
Crystal dimensions (mm)	0.25 × 0.50 × 0.50	0.20 × 0.30 × 0.40
Crystal system	monoclinic	monoclinic
Space group	$P2/n$	$P2_1/m$
Unit cell dimensions		
a (Å)	14.221(8)	9.056(3)
b (Å)	10.182(5)	13.978(4)
c (Å)	14.064(8)	9.553(3)
β (°)	93.42(2)	105.57(1)
V (Å^3)	2033(2)	1165(1)
Z	2	2
D_{calc} (g cm^{-3})	1.682	1.695
Radiation, Mo Kα (λ, Å)	0.71073	0.71073
Temperature (K)	298	298
Scan mode/speed (° min^{-1})	$\theta-2\theta/4.0$	$\theta-2\theta/4.2$
$2\theta_{max}$ (°)	50.0	50.0
Reflections collected	3479	3832
Unique reflections (R_{int})	3348 (0.0429)	2097 (0.0189)
Data with $I > 2\sigma(I)$	2742	2047
Parameters refined	289	214
$[\Delta/\sigma]_{max}$	0.593	0.060
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ (e Å^{-3})	0.981, −1.675	0.510, −1.025
w [a]	$a = 0.0466$, $b = 3.4504$	$a = 0.0309$, $b = 0.1058$
Goodness-of-fit (on F^2)	1.115	1.107
R_1 [b]	0.0359	0.0215
wR_2 [c]	0.1060	0.0539

[a] $w = 1/[\sigma^2(F_o^2)+(aP)^2+bP]$ and $P = (\max(F_o^2,0)+2F_c^2)/3$.
[b] $R_1 = \Sigma(|F_o|-|F_c|)/\Sigma(|F_o|)$.
[c] $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

3. Results and discussion

3.1. Synthetic comments and μ_{eff} values

The preparation of complexes **1**–**4** and **5**–**8** is summarised in Eqs. (1) and (2), respectively.

$$2LnCl_3\cdot 6H_2O + 6DMU \xrightarrow{EtOH} [Ln(DMU)_6][LnCl_6] + 12H_2O \qquad (1)$$

Ln = Pr (**1**), Nd (**2**), Gd (**3**), Er (**4**).

$$Ln(NO_3)_3\cdot 6H_2O + 3DMU \xrightarrow{EtOH} [Ln(NO_3)_3(DMU)_3] + 6H_2O \qquad (2)$$

Ln = Pr (**5**), Nd (**6**), Gd (**7**), Er (**8**).

Complexes **1**–**4** and **5**–**8** seem to be the only products from the $LnCl_3\cdot 6H_2O$–DMU and $Ln(NO_3)_3\cdot 6H_2O$–DMU (Ln = Pr, Nd, Gd, Er) reaction systems in alcohols (EtOH, MeOH). The DMU:Ln(III) reaction ratio has no influence on the identity of the complexes. Thus, despite our efforts we could not obtain neutral chloro complexes or cationic complexes with nitrates as counterions.

The experimental r.t. μ_{eff} values (Table 1) show very little deviation from the theoretical values (Pr(III), 3.58; Nd(III), 3.62; Gd(III), 7.94; Er(III), 9.6 B.M.) predicted by Eq. (3), suggesting that the 4f electrons in these complexed lanthanide ions are well-shielded by the outermost 5s and 5p electrons [47,48].

$$\mu_{eff} = g[J(J+1)]^{1/2} \qquad (3)$$

3.2. Description of structures

Selected bond distances and angles for complexes **2** and **6** are listed in Tables 3 and 4, respectively. ORTEP plots of the ions of complex **2** are shown in Figs. 2 and 3. The molecular structure of **6** is depicted in Fig. 4, while the coordination polyhedron of the Nd(III) atom is shown in Fig. 5.

Complex **2** crystallises in monoclinic space group $P2/n$. Its structure consists of isolated, almost perfect octahedral $[Nd(DMU)_6]^{3+}$ and $[NdCl_6]^{3-}$ ions. The Nd(III) atom of the cation sits on an inversion centre and is surrounded by six O-bonded DMU molecules. The average Nd–O distance (2.313 Å) is shorter than the La–O distance in the seven-coordinate complex $[La(O_2CMe)_3U]$ (2.461 Å, U = urea) [49,50] and slightly longer than the average Er–O bond length (2.251 Å) in the seven-coordinate complex $[Er(DMU)_6(H_2O)](ClO_4)_3$ [51]. The bond distance and angle features of the DMU ligands in **2** are comparable to those for DMU itself [52].

Table 3
Selected bond distances (Å) and angles (°) for the neodymium(III) complex **2**

$[Nd(DMU)_6]^{2+}$		$[NdCl_6]^{3-}$	
Bond distances			
Nd(1)–O(1)	2.317(3)	Nd(2)–Cl(1)	2.725(2)
Nd(1)–O(11)	2.313(3)	Nd(2)–Cl(2)	2.727(2)
Nd(1)–O(2)	2.310(3)	Nd(2)–Cl(3)	2.695(2)
C(2)–O(1)	1.261(5)		
C(12)–O(11)	1.265(6)		
C(22)–O(21)	1.252(5)		
C(2)–N(1)	1.328(7)		
C(2)–N(2)	1.330(7)		
C(12)–N(11)	1.334(8)		
C(12)–N(12)	1.313(8)		
C(22)–N(21)	1.320(7)		
C(22)–N(22)	1.315(7)		
Bond angles			
O(1)–Nd(1)–O(11)	91.0(1)	Cl(1)–Nd(2)–Cl(2)	87.6(1)
O(1)–Nd(1)–O(21)	92.0(1)	Cl(1)–Nd(2)–Cl(3)	91.8(1)
O(11)–Nd(1)–O(21)	92.1(1)	Cl(2)–Nd(2)–Cl(3)	88.2(1)
C(2)–O(1)–Nd(1)	164.0(3)		
C(12)–O(11)–Nd(1)	169.0(4)		
C(22)–O(21)–Nd(1)	164.9(3)		

Table 4
Selected bond distances (Å) and angles (°) for the neodymium(III) nitrate complex **6** [a]

Bond distances			
Nd–O(8)	2.324(2)	C(3)–N(2)	1.414(7)
Nd–O(9)	2.344(3)	C(1)–N(1)	1.422(9)
Nd–O(1)	2.529(2)	C(5)–N(3)	1.326(7)
Nd–O(3)	2.613(2)	C(5)–N(4)	1.270(6)
Nd–O(4)	2.573(2)	N(5)–O(1)	1.270(4)
Nd–O(6)	2.568(4)	N(5)–O(2)	1.230(4)
C(2)–O(8)	1.253(4)	N(5)–O(3)	1.242(4)
C(5)–O(9)	1.260(5)	N(6)–O(4)	1.247(2)
C(2)–N(1)	1.367(7)	N(6)–O(5)	1.225(4)
C(2)–N(2)	1.297(7)	N(7)–O(6)	1.244(3)
		N(7)–O(7)	1.232(4)
Bond angles			
O(8)–Nd–O(8) ≠ 1	149.5(1)	O(1)–Nd–O(6)	142.5(1)
O(8)–Nd–O(9)	91.7(2)	O(3)–Nd–O(4)	117.3(1)
O(8)–Nd–O(1)	82.6(1)	O(3)–Nd–O(6)	149.1(1)
O(8)–Nd–O(3)	75.1(1)	O(4)–Nd–O(4) ≠ 1	48.8(1)
O(8)–Nd–O(4)	76.1(1)	O(4)–Nd–O(6)	71.2(1)
O(8)–Nd–O(4) ≠ 1	123.9(1)	O(4)–Nd–O(6) ≠ 1	91.0(1)
O(8)–Nd–O(6)	78.9(1)	O(6)–Nd–O(6) ≠ 1	48.7(1)
O(8)–Nd–O(6) ≠ 1	127.1(1)	C(2)–O(8)–Nd	157.6(2)
O(8) ≠ 1–Nd–O(9)	71.8(2)	C(5)–O(9)–Nd	171.5(6)
O(9)–Nd–O(1)	131.7(1)	O(1)–N(5)–O(2)	120.5(3)
O(9)–Nd–O(3)	83.0(1)	O(1)–N(5)–O(3)	116.8(3)
O(9)–Nd–O(4)	151.5(1)	O(2)–N(5)–O(3)	122.7(3)
O(9)–Nd–O(4) ≠ 1	141.6(2)	O(4)–N(6)–O(4) ≠ 1	116.8(3)
O(9)–Nd–O(6)	81.4(1)	O(4)–N(6)–O(5)	121.6(1)
O(9)–Nd–O(6) ≠ 1	75.8(1)	O(6)–N(7)–O(6) ≠ 1	116.7(3)
O(1)–Nd–O(3)	49.2(1)	O(6)–N(7)–O(6)	121.7(1)
O(1)–Nd–O(4)	72.9(1)		

[a] Symmetry transformations used to generate equivalent atoms: ≠ 1 x, $-y+1/2$, z.

Due to coordination the average C=O bond distance in **2** (1.259 Å) is slightly longer than the C=O bond length in free DMU (1.242 Å) [52]; the amide-type C–N bonds are short (average 1.323 Å), as expected for the amide resonance [53]. There are two (symmetry equivalent) intracationic C(13)–H···O(21) interactions that can be regarded as weak hydrogen bonds, see Table 5. Interactions of the C–H···(O,N) type are correctly termed hydrogen bonds because they are, like the (N,O)–H···(N,O) hydrogen bonds, largely electrostatic in character [3]. Weak hydrogen bonds with C–H groups as donors are currently under intense study. Formely considered 'unusual' or 'nonconventional', they are now discussed rather frequently in many fields of structural chemistry [3,7,54–56] and biology [57]. Typical H···O(N) separations occur in the 2.2–3.0 Å range and the hydrogen bond angle is in the 100–180° range [3], while dissociation energies are 0.4–4 kcal mol^{-1}, with the majority <2 kcal mol^{-1} [54].

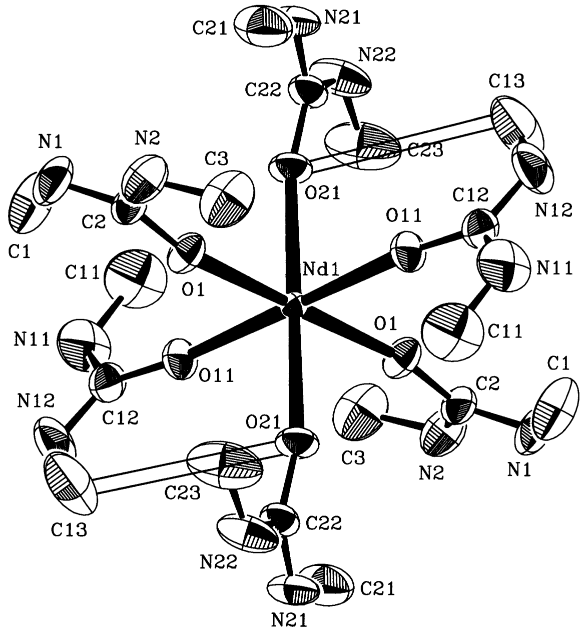

Fig. 2. ORTEP plot of the cation $[Nd(DMU)_6]^{3+}$ present in the crystal structure of complex **2**. An identical numbering scheme is used for atoms generated by symmetry. The intracationic hydrogen bonds are shown.

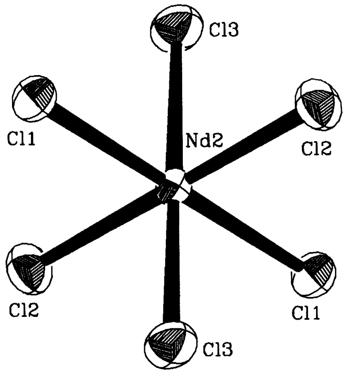

Fig. 3. ORTEP plot of the anion $[NdCl_6]^{3-}$ present in the crystal structure of complex **2**. An identical numbering scheme is used for atoms generated by symmetry.

The Nd(III) atom of the $[NdCl_6]^{3-}$ anion also sits on an inversion centre. The Nd–Cl distances (average 2.716 Å) compare very well with similar distances found for the two $[NdCl_6]^{3-}$ ions (average distances 2.721 and 2.706 Å) that are present in the crystal structure of $Cs_3[NdCl_6]$ [58]; the latter consists of distorted octahedra around Nd(III) with the Cs^+ ions acting as bulky counterions. The Nd–Cl bond lengths of **2** are also very similar to those found for the octahedral $[NdCl_6]^{3-}$ ion in $(MeNH_3)_8[NdCl_6][NdCl_4(H_2O)_2]_2Cl_3$ (average 2.711 Å) [59]. The Cl–Nd–Cl angles are fairly close to 90°, indicating only a slight distortion of the octahedral coordination sphere.

The structure of **6** consists of mononuclear $[Nd(NO_3)_3(DMU)_3]$ molecules. There is a mirror plane passing through the metal ion and atoms O(1), O(2), O(3), N(5) defining one nitrato ligand, while the same mirror plane is bisecting the other two nitrates passing

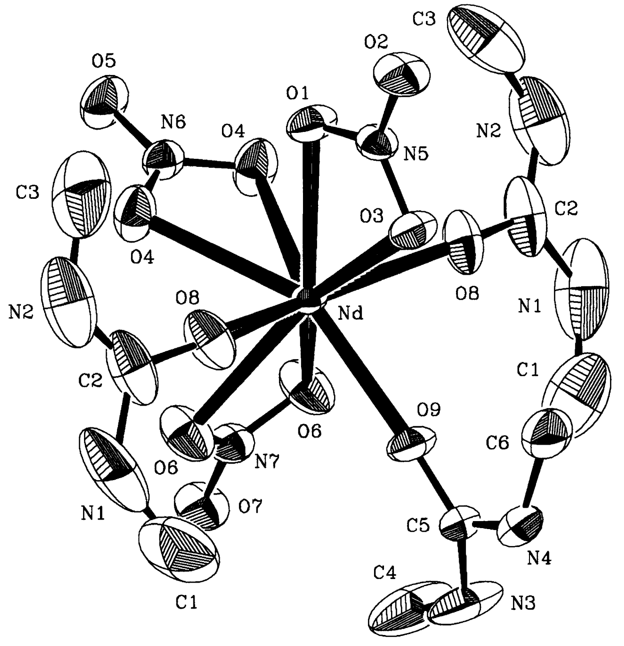

Fig. 4. Molecular structure of **6**. An identical numbering scheme is used for atoms generated by symmetry.

Table 5
Dimensions of the unique hydrogen bonds (distances in Å and angles in °) for complex **2**

D–H···A	D···A	H···A	∠DHA	Symmetry equivalence of A
N(1)–H(N1)···Cl(1)	3.525	2.726	146.5	x, y, z
N(2)–H(N2)···Cl(1)	3.340	2.493	169.0	x, y, z
N(11)–H(N11)···Cl(2)	3.329	2.514	176.3	$3/2-x, -1+y, 1/2-z$
N(21)–H(N21)···Cl(2)	3.402	2.695	141.5	$1-x, -y, 1-z$
N(22)–H(N22)···Cl(3)	3.375	2.689	140.6	$x, y, 1+z$
C(1)–H(1A)···Cl(3)	3.650	2.80	142	$1-x, -y, -z$
C(13)–H(13B)···O(21) [a]	3.611	2.55	147	$1-x, -1-y, 1-z$
C(23)–H(23B)···Cl(3)	3.609	2.78	133	$3/2-x, y, 1/2-z$

A, acceptor; D, donor.
[a] Intracationic hydrogen bond.

through atoms O(5), N(6) and O(7), N(7). As a consequence of the molecular symmetry implied by the above described mirror plane, the two DMU molecules are symmetrically related whilst the third DMU molecule [the one containing O(9)] is disordered above and below the mirror plane. The Nd(III) atom is in a nine-coordinate environment comprising six oxygens from the three symmetrically chelating nitrato groups and the oxygens from the three monodentate DMU ligands. The $\mathrm{Nd{-}O_{NO_3^-}}$ bond lengths are in the 2.529(2)–2.613(2) Å range. They are comparable to those [2.485(19), 2.600(15) Å] in the nine-coordinate complex $[Nd_2(O_2CMe)_4(NO_3)_2(phen)_2]$ (phen = 1,10-phenanthroline) which contains also bidentate chelating nitrates [60]. The average $\mathrm{Nd{-}O_{NO_3^-}}$ distance in **6** (2.571 Å) is slightly shorter than that in the ten-coordinated complex $[Nd(NO_3)_3U_2(H_2O)_2]$ (2.597 Å, U = urea) [61], as expected from the lower coordination number of the Nd(III) atom in the former.

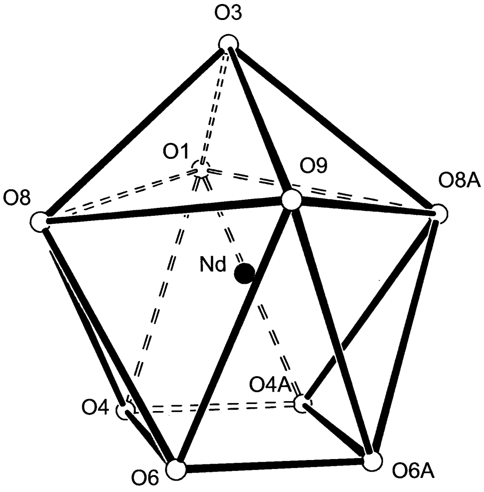

Fig. 5. A view of the coordination polyhedron of **6** showing the distorted square monocapped antiprismatic coordination of the Nd(III) ion. Symbols A are used for symmetry related (x, $-y+1/2$, z) donor atoms.

The polyhedron of the Nd(III) coordination sphere conforms to neither of the common geometries for a nine-coordinate environment, viz. tricapped trigonal prismatic or monocapped square antiprismatic [62]. Presumably the small ‘bite’ of the nitrates is primarily responsible for this feature. However, the polyhedron comes closer to a distorted monocapped square antiprism with one of the nitrate oxygens, O(3), forming the cap of the ‘square’ O(1)O(8)O(9)O(8) ≠ 1 base (Fig. 5). It should be emphasised that from the N(5)O(1)O(2)O(3) nitrate donor atoms, the capping atom forms a weaker bond to neodymium(III) [2.613(2) Å] than the noncapping atom [Nd–O(1) = 2.529(2) Å]. In this particular case, the geometry can be also described in terms of a pseudo six-coordinate species in which each of the nitrates is considered as occupying a single coordination position [63]. The geometry of this coordination polyhedron, consisting of the three DMU O atoms and the three nitrate N atoms, is distorted *mer* octahedral.

All DMU ligands in **2** and **6** are coordinated in a rather linear fashion, with Nd–O–C angles ranging from 157.6(2) to 171.5(6) Å. Linearly or approximately linearly coordinated urea or urea derivatives are extremely unusual and have been observed only in few cases [42,49,64]. The bent mode is the usual way of coordination of ureas [31,32,49]. The rare linear behaviour has been discussed for complex $[MnBr_2(DMU)_3]$

by Delaunay and Hugel in terms of electronic structure and π-acceptor capacity of the planar DMU ligand [64].

Complexes **2** and **6** join a small family of structurally characterised metal complexes of DMU [31,32,42,51,64,65]. The only other structurally characterised lanthanide(III) complex of DMU is $[Er(DMU)_6(H_2O)](ClO_4)_3$ [51].

We have up to now discussed aspects of the molecular structures of complexes **2** and **6**. Figs. 6 and 8 provide views of the hydrogen bonded networks of the complexes. Distances and angles for the interionic (**2**) and intermolecular (**6**) hydrogen bonds present in the crystal structures are listed in Tables 5 and 6, respectively.

The $[Nd(DMU)_6]^{3+}$ cations and $[NdCl_6]^{3-}$ anions self-assemble to form a hydrogen bonded 3D architecture in **2**. All chlorides from $[NdCl_6]^{3-}$ act as hydrogen bond acceptors to NH groups from DMU ligands; ten out of 12 NH groups participate in hydrogen bonds. In addition, there are two crystallographically unique C–H···Cl hydrogen bonds. Hydrogen bonds with halogen acceptors are of recent interest [20,54,66]. A metal-bound halogen atom is strongly polar and a good acceptor. The electronic structure suggests different basicity characteristics of the different electron lone pairs (Fig. 7) [67], and indeed, X–H···Cl–M hydrogen bonds in molecular crystals (including **2**) are almost exclusively donated roughly perpendicular to the M–Cl bond (angular range 80°–140°) [67,68].

The $[Nd(NO_3)_3(DMU)_3]$ molecules in **6** are arranged in infinite 3D networks through five, crystallographically independent, intermolecular N–H···O(NO_3^-) hydrogen bonds. All NH groups participate in H bonds. Two nitrato ligands accept hydrogen bonds only through their non-coordinated oxygen atoms [O(5), O(7)], while the third nitrate participates in two hydrogen bonds using two oxygen atoms, including a coordinated one [O(1)]. There are three intralayer hydrogen bonds, i.e. N(3)–H···O(1), N(3)–H···O(2) and N(4)–H···O(7), responsible for the formation of layers parallel to the *ac* plane. The remaining two, crystallographically independent, N–H···O(NO_3^-) hydrogen bonds [N(1)–H···O(7), N(2)–H···O(5)] link the layers together resulting in the formation of the 3D network.

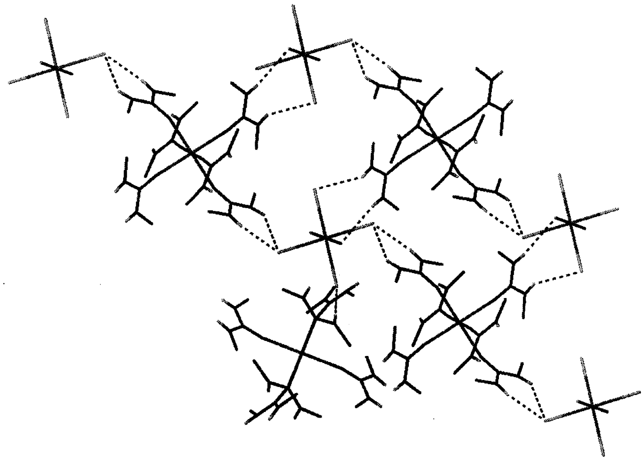

Fig. 6. A view of the *bc* plane in the crystal structure of complex **2** showing all unique interionic hydrogen bonds; the C–H···Cl hydrogen bonds are not shown.

Table 6
Dimensions of the unique hydrogen bonds (distances in Å and angles in °) for complex **6**

D–H···A	D···A	H···A	∠DHA	Symmetry equivalence of A
N(1)–H(N1)···O(7)	3.114	2.511	155.9	$-x, -y, -z$
N(2)–H(N2)···O(5)	3.089	2.185	153.2	$-x, -y, 1-z$
N(3)–H(N3)···O(1)	2.933	2.278	122.9	$x, y, -1+z$
N(3)–H(N3)···O(2)	3.361	2.479	148.8	$x, y, -1+z$
N(4)–H(N4)···O(7)	3.081	2.415	134.2	$1+x, y, z$

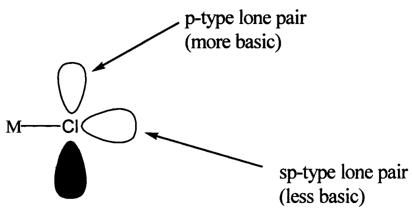

Fig. 7. The electron lone pairs on metal-bonded chloride [54].

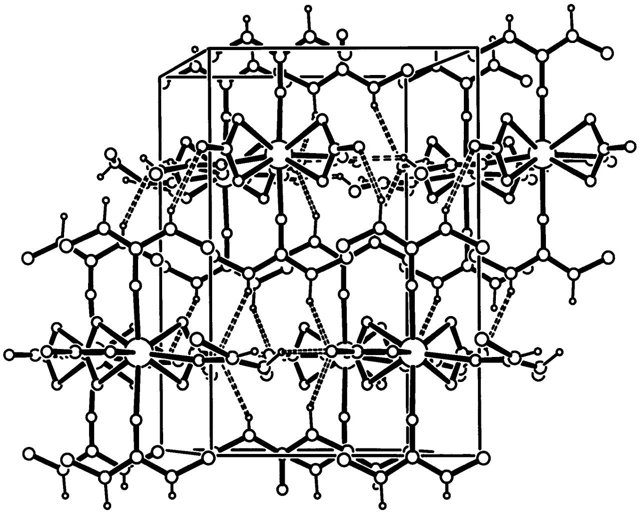

Fig. 8. Packing diagram of the crystal structure of **6** showing the 3D network formed by the intermolecular N–H···O(NO_3^-) hydrogen bonds (orientation: *a* towards the reader, *c* to the right).

Most interionic N–H···Cl and the intermolecular N–H···O(NO_3^-) hydrogen bonds in the supramolecular structures of **2** and **6**, respectively, can be regarded as 'moderate' [54].

3.3. Spectroscopic studies

The full vibrational analysis of crystalline DMU has been published [41]. Table 7 gives diagnostic IR bands of the free ligand and the representative complexes $[\mathrm{Er(DMU)_6}][\mathrm{ErCl_6}]$ (**4**) and $[\mathrm{Nd(NO_3)_3(DMU)_3}]$ (**6**); Raman metal–ligand stretching vibrations also appear in Table 7. Assignments have been given in comparison with the data obtained for free, i.e. uncoordinated, DMU [41] and its 3d-metal complexes [31,32,42,64], by noting the appearance of new bands in **6** (due to nitrate vibrations) and in the low-frequency spectra of both complexes (due to metal–ligand vibrations), and by studying extensive literature reports [69–74].

The IR spectra (4000–400 cm^{-1}) of the four chloro complexes **1**–**4** are identical and, thus, we believe that all four complexes have a similar structure in the solid state; analogous arguments apply for the nitrato complexes **5**–**8**.

The bands with $\nu(\mathrm{CN})_{\mathrm{amide}}$ character are situated at slightly higher frequencies in the spectra of **1**–**8** than for free DMU, whereas the ν(CO) band shows a frequency decrease. These shifts are consistent with oxygen coordination, suggesting the presence of $^{+}\mathrm{N{=}C{-}O}^{-}$ resonant forms [50,64,69,70]. Upon coordination via oxygen, the positively charged lanthanide(III) ion stabilises 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, while the double bond character of the CO bond decreases, resulting in an increase of the CN stretching frequency and a decrease in the CO stretching frequency, respectively [64].

The cited nitrate frequencies in Table 7 arise from spectra obtained as Nujol and hexachlorobutadiene mulls, since it is well known that pressing a KBr pellet affects the nitrate coordination [71] (the ligand's frequencies are identical in both the KBr and mull spectra). The nitrate vibrations in the mull spectra of **5**–**8** are indicative of the presence of bidentate nitrato groups, because [70,72] the separation of the two highest-frequency bands $\nu_1(\mathrm{A_1})$ and $\nu_5(\mathrm{B_2})$ [under C_{2v} symmetry] is large ($\sim$ 320 cm^{-1}). The IR spectra of **5**–**8** in KBr are indicative of the simultaneous presence of bidentate and ionic nitrates; the existence of the latter is deduced from the appearance of the $\nu_3(\mathrm{E}')$ $[\nu_{\mathrm{d}}(\mathrm{NO})]$ mode of the D_{3h} ionic nitrate at $\sim$ 1390 cm^{-1} [71,72], suggesting that a certain amount of nitrato ligands are replaced by bromides in the KBr matrix.

The appearance of one IR-active $\nu(\mathrm{Ln{-}O})$ $[F_{1\mathrm{u}}$ under $O_h]$, two Raman-active $\nu(\mathrm{Ln{-}O})$ $[A_{1\mathrm{g}}, E_{\mathrm{g}}$ under $O_h]$, one IR-active $\nu(\mathrm{Ln{-}Cl})_{\mathrm{t}}$ $[F_{1\mathrm{u}}$ under $O_h]$ and two Raman-active $\nu(\mathrm{Ln{-}Cl})_{\mathrm{t}}$ $[F_{1\mathrm{u}}$ under $O_h]$ vibrations at $\sim$ 335, 345–315, $\sim$ 295 and 305–280 cm^{-1}, respectively, in the spectra of **1**–**4** reflects the octahedral stereochemistry of the $[\mathrm{Ln(DMU)_6}]^{3+}$ and $[\mathrm{LnCl_6}]^{3-}$ ions [70,73]. The $\mathrm{Nd{-}O_{NO_3^-}}$ stretching vibrations appear at 245–190 cm^{-1} [73,74]; their frequencies are lower than those of the $\mathrm{Ln{-}O_{DMU}}$ stretching vibrations. Neither a systematic increase in the frequency of the metal–ligand

Table 7
Most characteristic and diagnostic vibrational [a] data (cm^{-1}) of free [b] DMU, and its representative complexes $[\mathrm{Er(DMU)_6}][\mathrm{ErCl_6}]$ (**4**) and $[\mathrm{Nd(NO_3)_3(DMU)_3}]$ (**6**)

Assignment	DMU	**4**	**6**
$\nu(\mathrm{NH})$	$\sim$ 3350sb	3372s, 3345sh	3388s, 3330sb
$\nu(\mathrm{CO})$	1628s	1606sb	1608sb
$\delta_{\mathrm{as}}(\mathrm{NH})$	1591s	1632sh	1635sh
$\nu_1(\mathrm{A_1})_{\mathrm{NO_3^-}}$ [c]			1622s
$\delta_{\mathrm{s}}(\mathrm{NH})$	1541m	1512m	1504s
$\nu_{\mathrm{as}}(\mathrm{CN})_{\mathrm{amide}}$ [d]	1270sb	1316m	
$\nu_{\mathrm{as}}(\mathrm{CN})_{\mathrm{amide}}$ [d] $+\nu_5(\mathrm{B_2})_{\mathrm{NO_3^-}}$ [c]			1302sh, 1294sb
$\rho_{\mathrm{as}}(\mathrm{CH_3})$	1195m	1196m	1204w
$\nu_{\mathrm{s}}(\mathrm{N{-}CH_3})$	1175m	1174m	1176s
$\nu_{\mathrm{as}}(\mathrm{N{-}CH_3})$	1040m		
$\nu_{a\mathrm{s}}(\mathrm{N{-}CH_3})+\nu_2(\mathrm{A_1})_{\mathrm{NO_3^-}}$ [c]			1036s
$\nu_{\mathrm{s}}(\mathrm{CN})_{\mathrm{amide}}$ [d]	931m	940m	936m
$\pi(\mathrm{CO})$	775m	762m	764m
$\nu_3(\mathrm{A_1})_{\mathrm{NO_3^-}}$ [c]			748s
$\pi_{\mathrm{as}}(\mathrm{NH})$	576mb	632mb	638sb
$\nu(\mathrm{Ln{-}O_{DMU}})$		334m 341w(R), 320m(R)	335m, 323w 338w(R), 321m(R)
$\nu(\mathrm{Er{-}Cl})_{\mathrm{t}}$		295s 303m(R), 288m(R)	
$\nu(\mathrm{Nd{-}O_{NO_3^-}})$			232m, 200w, 191m 240m(R), 212w(R)

Abbreviations: b, broad; m, medium; s, strong; sh, shoulder; w, weak.

[a] All bands are IR bands, except those designated by R which are Raman bands.

[b] In its *Cc* crystal phase.

[c] The cited wavenumbers of the nitrato ligands arise from spectra recorded as Nujol and hexachlorobutadiene mulls (see text).

[d] These modes refer to the –NH–CO–NH– group.

stretching vibrations with decreasing metal ion radius from Pr(III) to Er(III)—which would indicate stronger lanthanide–ligand bonds—nor an abrupt frequency increase of these vibrations in **3** and **7**—that could be attributed to stabilisation caused by the half-filled 4f shell of Gd(III) [75]—were observed. This is most probably due to the fact that the lanthanide–ligand stretching modes in **1**–**8** are not 'pure' vibrations.

4. Conclusions and perspectives

The LnX_3–DMU chemistry (Ln = lanthanide; X = Cl, NO_3) described here has fulfilled its promise as a source of interesting hydrogen bonded 3D networks based on simple metal complexes. In the case of the chloro complexes **1**–**4**, this work has shown that the hexakis(*N*,*N′*-dimethylurea)lanthanide(III) cations can act as hydrogen-bonding building blocks with multi-fold connectivity linking $[LnCl_6]^{3-}$ to generate 3D architectures. We are presently pursuing our prediction that these cations will form hydrogen bonding contacts to a variety of bulky inorganic and organic anions to generate a rich diversity of networks. We have also shown that the hydrogen bonding functionalities on the molecules of tris(*N*,*N′*-dimethylurea)trinitratolanthanides(III) (**5**–**8**) have yielded 3D architectures without the intervention of anionic intermediaries. We currently work on other neutral lanthanide(III) complexes of DMU using pseudohalides as coligands to take advantage of the fact that these ligands have a poor ability to participate in hydrogen bonds, thus favouring DMU–DMU hydrogen bonded assemblies.

The role of metal ions in supramolecular systems may simply be to act as a coordination centre providing a template for the formation of a rigid framework of remote hydrogen bonding sites [19]. Alternatively, the metal ion may exert an electronic effect on the individual proton donor and acceptor sites, influencing the hydrogen bonding in a more subtle manner [19]. Let us now briefly discuss some differences in the supramolecular structures of 3d- and 4f-metal ion complexes of DMU.

The N–H hydrogens of symmetrical disubstituted ureas prefer to adopt an *anti*, *anti* (or *trans*, *trans* [41]) relationship to the carbonyl group and to form three-centre bonds to urea carbonyl groups [7,39], see Fig. 1. Coordination of DMU to 3d-metals in complexes containing $[M(DMU)_6]^{2+}$ cations (Fig. 9) (M = Mn, Co, Ni, Zn) and monoanionic counter ions [31,32] has two consequences. First, while both lone pairs on the carbonyl oxygen atom of free DMU [41,52] act as hydrogen bond acceptors, in the complexes one pair acts as a 'moderate' [54] hydrogen bond acceptor and the other participates in the formation of the M–O coordination bond. Second, the N–H hydrogens of each coordinated DMU adopt a *syn*, *anti* (or *cis*, *trans*) relationship to the coordinated carbonyl groups. The *syn* (or *cis*) configuration of one NH group is necessary for the formation of six-membered-ring intracationic hydrogen bonds; these hydrogen bonds create six six-membered pseudochelating MOCNH···O rings per M(II) atom, giving an extra stabilisation to the $[M(DMU)_6]^{2+}$ cation. The configuration of the other NH group remains *anti* (or *trans*) relative to the carbonyl group to participate in intermolecular (interionic) hydrogen bonds with the counter ions. Coordination of DMU to 4f-metals in complexes **1**–**4**, which also contain the hexakis(*N*,*N′*-dimethylurea)metal cation (and, thus, comparisons with 3d-metals are more valid), has different consequences. First, there is no electron pair on the carbonyl oxygen atom of DMU that acts as a hydrogen bond acceptor [with the exception of the weak C(13)–H(13B)···O(21) intracationic hydrogen bond]. Second, the N–H hydrogens of each coordinated DMU adopt an *anti*, *anti* (or *trans*, *trans*) relationship to the carbonyl group (like in free DMU [41,52]) to participate in intermolecular (interionic) hydrogen bonds with the chlorides of $[NdCl_6]^{3-}$. The size and the charge of both the cation and the anion are surely among the factors that contribute to the observed differences; however, more chemistry is needed to evaluate the relative importance of each factor.

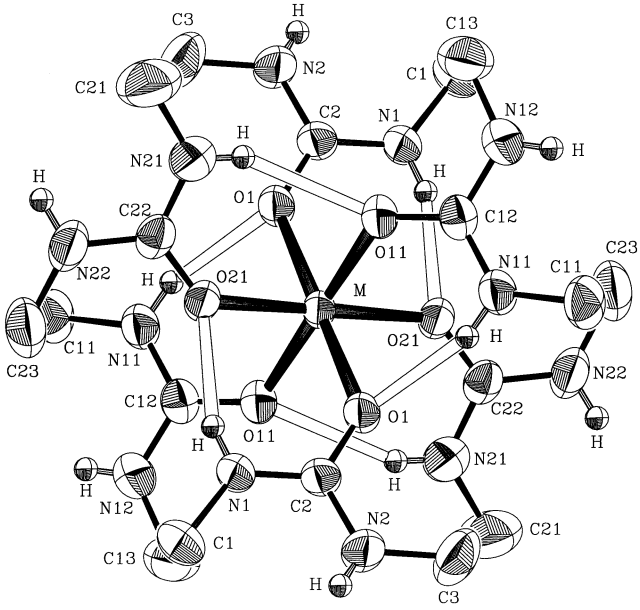

Fig. 9. A general ORTEP representation of the centrosymmetric cations $[M(DMU)_6]^{2+}$ (M = Mn, Co, Ni, Zn) present in the structures of many cationic complexes with various counter ions [31,32]. Open bonds indicate intramolecular (intracationic) hydrogen bonds (see text for further discussion). An identical numbering scheme is used for atoms generated by symmetry.

Another difference between the chemistries of the M(II)–DMU (M = Mn, Co, Ni, ...) and Ln(III)–DMU systems—that leads to different structural motifs—is the fact that the more oxophilic lanthanide ions interact strongly with the nitrates (complexes **5**–**8**), whereas the latter remain uncoordinated in $[M(DMU)_6](NO_3)_2$ (M = Co, Ni, Cu, Zn) [32,76].

In a recent review [20], Beatty emphasised that despite all the possible intermolecular interactions (ligand–solvent, ligand–counter ion, ligand–metal) that are present in solution, ligand–ligand hydrogen bonds can be reliable, reproducible, dominating steering forces for the supramolecular assembly of coordination complexes. Our results at the time of writing indicate that 4f-metal ions and *N*,*N*′-disubstituted ureas prove to be central players in the field of hydrogen bonded networks of coordination complexes.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 189968 and 189969 for complexes **2** and **6**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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