

The Hexakis(N,N'-dimethylurea)cobalt(II) Cation: A Flexible Building Block for the Construction of Hydrogen Bonded Networks

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The ligand N,N'-dimethylurea (DMU) is used to propagate the octahedral coordination geometry of $[\text{Co}(\text{DMU})_6]^{2+}$ into 1D and 2D assemblies *via* a combination of coordinative bonds and interionic hydrogen-bonding. Compounds $[\text{Co}(\text{DMU})_6](\text{ClO}_4)_2$ (**1**), $[\text{Co}(\text{DMU})_6](\text{BF}_4)_2$ (**2**) and $[\text{Co}(\text{DMU})_6](\text{NO}_3)_2$ (**3**) have been prepared from the reactions of DMU and the appropriate hydrated cobalt(II) salts in EtOH, MeCN or Me₂CO (only for **1**) in the presence of 2,2-dimethoxypropane. Crystal structure determinations demonstrate the existence of $[\text{Co}(\text{DMU})_6]^{2+}$ cations and ClO_4^- , BF_4^- or NO_3^- counterions. The great stability of the $[\text{Co}(\text{DMU})_6]^{2+}$ cation in the solid state is attributed to a *pseudochelate* effect which arises from the existence of strong intracationic N-H...O(DMU) hydrogen bonds. The $[\text{Co}(\text{DMU})_6]^{2+}$ cations and counterions self-assemble to form a hydrogen-bonded 1D architecture in **1**, and different 2D hydrogen-bonded networks in **2** and **3**. The precise nature of the resulting supramolecular structure is influenced by the nature of the counterion. Two main motifs of intermolecular (interionic) hydrogen bonds have been observed: N-H...O(ClO_4^- , NO_3^-) or N-H...F(BF_4^-) and weak C-H...F(BF_4^-) or C-H...O(NO_3^-) hydrogen bonds. The complexes were also characterized by vibrational spectroscopy (IR, far-IR, low-frequency Raman). The spectroscopic data are discussed in terms of the nature of bonding and the known structures.

Key words: Cobalt(II)/N,N'-Dimethylurea Complexes, Hydrogen-Bonded Coordination Complexes, Vibrational Spectroscopy

Introduction

Recent efforts in the field of crystal engineering have focused on the predictable assembly of *organic* molecular solids via intermolecular interactions [1 - 5] and it has become clear that certain functional groups, e. g. carboxylic acids, amides and ureas, are reliable, robust connectors for the formation of hydrogen-bonded organic networks [1, 2, 6 - 9]. However, little work has been done in constructing assemblies of coordination compounds via directional intermolecular interactions [10 - 18]. 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 certain coordination geometry [11]. A specific geometry can then be propagated throughout the crystal

structure by attaching substituents to the ligands; these substituents act as intermolecular connectors. Ordered assemblies of transition metal complexes (coordination polymers), *i. e.* supramolecular systems involving coordinative connectivities, attract intense research due to their potential as useful porous, conductive and magnetic molecular materials [19 - 22].

We have recently [23, 24] 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 [25 - 28]. Remarkable analogies can be drawn [29] between hydrogen-bonded networks and coordination polymers. For hydrogen-bonded networks, the donor (*i. e.*, a protic hydrogen atom) and the

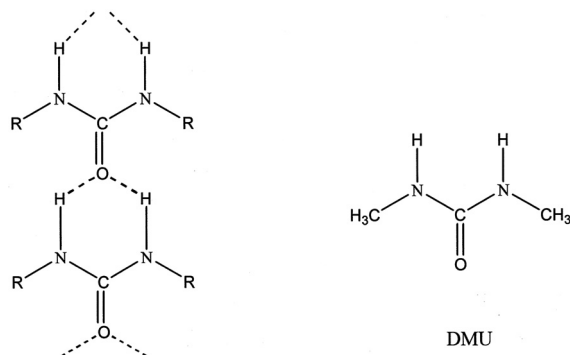


Fig. 1. A small part (which contains only two molecules) of the α -network commonly observed in symmetrically disubstituted ureas (left) and the chemical formula of N,N'-dimethylurea, abbreviated as DMU.

acceptor (*i.e.*, a region of high electron density) can be compared with metal ions and ligands, respectively. Furthermore, as noted by Etter [30], in cases where there are multiple hydrogen-bonding sites, there is a rather high degree of predictability concerning which donors and acceptors will be engaged. Therefore, the “node and spacer” approach can be employed equally well with hydrogen bonds as with coordinative bonds [29]. 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. Available strategies for the achievement of this goal have been recently reviewed [13].

Ureas have been among the central players in organic crystal engineering [1, 6, 31 - 33]. In particular, symmetrically disubstituted ureas form α -networks with each urea molecule donating two hydrogen bonds and “chelating” the carbonyl oxygen atoms of the next molecule in the network (Fig. 1). This paper describes the full spectroscopic and structural characterization of the products from the reactions between cobalt(II) perchlorate, tetrafluoroborate and nitrate with N,N'-dimethylurea (DMU, Fig. 1).

Results and Discussion

Preliminary considerations

In contrast to the great number of studies concerning free ureas [1, 6, 31 - 34], little is known about the supramolecular architectures based on hydrogen-

bonding interactions between simple metal-urea complexes. We currently study the supramolecular structures of simple metal-DMU complexes where, in principle, the oxygen atom of DMU can coordinate to the metal ion and/or provide a hydrogen bonding acceptor site. We hope that by reacting metal ions with a ligand that contains both an efficient coordination site and two hydrogen bonding functionalities, assembly can be dictated by intermolecular hydrogen bonding interactions. At the outset of our efforts we would like to reduce the possibility of coordination polymer formation through anionic ligands; for this reason, we employ metal sources containing weakly coordinating anions such as ClO_4^- , BF_4^- , NO_3^- *etc.* Thus, infinite assemblies based on ligand-counterion hydrogen bonds are expected, though these are not, strictly speaking, ligand-based hydrogen-bonded assemblies.

In a recent paper, we described the preparation and crystal structures of complexes $[\text{M}(\text{DMU})_6](\text{ClO}_4)_2$ ($\text{M} = \text{Mn}, \text{Ni}, \text{Zn}$) and $[\text{Cu}(\text{OCIO}_3)_2(\text{DMU})_4]$ [24]. The $[\text{M}(\text{DMU})_6]^{2+}$ cations and ClO_4^- anions self-assemble to form a hydrogen bonded 1D architecture in the manganese(II) complex and different 2D hydrogen-bonded networks in nickel(II) and zinc(II) complexes; the hydrogen bonding functionalities on the molecules of the copper(II) complex create a 2D structure. In order to also investigate the influence of the steric requirements and hydrogen bonding ability of the counterion on the supramolecular assembly, in the present study the metal ion (Co^{II}) is kept constant while the counter ion is varied. Powders with compositions $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{DMU}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{DMU}$ had been reported in the old literature [35 - 37], but neither the crystal structures nor detailed spectroscopic data on these compounds were available prior to this work.

The present work can be also regarded as a continuation of our efforts in the spectroscopy of free ureas [38, 39] and in the study of their coordination chemistry [40 - 43].

Synthetic comments

The preparation of the three complexes reported in this work is summarized in eq. (1):

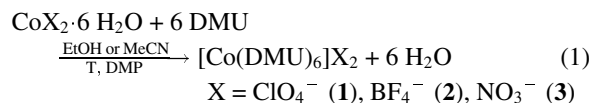


Table 1. Selected bond lengths (Å) and angles (°) for the $[\text{Co}(\text{DMU})_6]^{2+}$ cations present in complexes **1**, **2** and **3**. The atoms C(2), C(12) and C(22), which are not labelled in Fig. 2, are the carbonyl carbon atoms of the three crystallographically independent DMU molecules.

	1	2	3
Co-O(1)	2.098(3)	2.091(2)	2.092(2)
Co-O(11)	2.104(3)	2.091(2)	2.089(2)
Co-O(21)	2.111(3)	2.098(2)	2.106(2)
C(2)-O(1)	1.272(4)	1.257(2)	1.265(3)
C(2)-N(1)	1.330(5)	1.329(3)	1.329(3)
C(2)-N(2)	1.324(5)	1.325(3)	1.327(3)
C(12)-O(11)	1.256(4)	1.262(3)	1.261(3)
C(12)-N(11)	1.329(5)	1.322(3)	1.332(3)
C(12)-N(12)	1.340(5)	1.334(3)	1.339(3)
C(22)-O(21)	1.264(5)	1.254(3)	1.254(3)
C(22)-N(21)	1.338(5)	1.329(3)	1.336(4)
C(22)-N(22)	1.334(5)	1.338(3)	1.334(3)
O(1)-Co-O(11)	92.6(1)	92.6(1)	92.4(1)
O(1)-Co-O(21)	91.5(1)	91.5(1)	88.8(1)
O(11)-Co-O(21)	91.2(1)	91.3(1)	88.7(1)
C(2)-O(1)-Co	130.9(2)	131.1(1)	131.0(1)
C(12)-O(11)-Co	128.7(2)	128.4(1)	126.1(2)
C(22)-O(21)-Co	130.3(2)	130.1(1)	131.7(2)

The employment of 2,2-dimethoxypropane (DMP, a known dehydrating agent) under heating was necessary to eliminate the possibility of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ formation in solution.

Complexes **1** and **2** seem to be the only products from the $\text{CoX}_2 \cdot 6\text{H}_2\text{O}/\text{DMU}$ reaction systems ($\text{X} = \text{ClO}_4, \text{BF}_4$). The solvent (EtOH, MeCN and even Me_2CO in the case of **1**) and the $\text{DMU}:\text{Co}^{\text{II}}$ reaction ratio (8:1, 6:1, 4:1, 3:1) have no influence on the identity of the complexes. The $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{DMU}$ reaction mixtures in EtOH, Me_2CO and MeCN at low $\text{DMU}:\text{Co}^{\text{II}}$ ratios (2:1, 1:1) behave in a different manner from those at high ligand:metal ratios (8:1, 6:1); the former repeatedly gave a mixture of a red oil and a powder of uncertain nature.

Description of structures

Selected bond distances and angles for the $[\text{Co}(\text{DMU})_6]^{2+}$ cations of complexes **1**, **2** and **3** are listed in Table 1. An ORTEP plot of the $[\text{Co}(\text{DMU})_6]^{2+}$ cations of complexes **1** and **2** is shown in Fig. 2; since the cations of these complexes are almost identical only one plot is given. The structure of $[\text{Co}(\text{DMU})_6]^{2+}$ present in the nitrate complex **3** is depicted in Fig. 3. Details of the

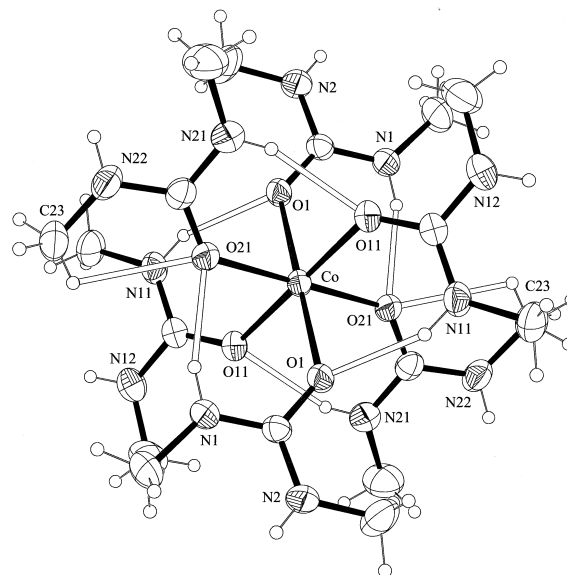


Fig. 2. An ORTEP representation of the cation $[\text{Co}(\text{DMU})_6]^{2+}$ present in complexes **1** and **2**. Open bonds indicate intramolecular (intracationic) hydrogen bonds. An identical labelling scheme is used for atoms generated by symmetry. For clarity, most carbon atoms are not labelled.

hydrogen bonds of **1**, **2** and **3** are provided in Tables 2, 3 and 4 respectively.

Complexes **1**, **2** and **3** crystallize in the triclinic space group $P\bar{1}$. Their structures consist of almost perfect octahedral $[\text{Co}(\text{DMU})_6]^{2+}$ cations and ClO_4^- , BF_4^- or NO_3^- counterions. The Co^{II} atom sits on an inversion centre and is surrounded by six O-bonded DMU ligands. The bond angles around the metal ion are fairly close to 90° , indicating only a slight distortion of the octahedral coordination sphere. There are six intramolecular (intracationic) hydrogen bonds with atoms N(1), N(11) and N(21) [and their symmetry equivalents] as donors, and atoms O(21), O(1) and O(11) [and their symmetry equivalents] as acceptors. These are regarded as “moderate” hydrogen bonds using Jeffrey’s [44] and Steiner’s [45] classifications. Additionally, in complexes **1** and **2** there are two (symmetry equivalent) intracationic C(23)-H \cdots O(21) interactions that can be regarded as weak hydrogen bonds. Interactions of the C-H \cdots (O, N) type are correctly termed hydrogen bonds because they are, like the (N, O)-H \cdots (N, O) hydrogen bonds, largely electrostatic in character [1]. Weak hydrogen bonds with C-H groups as donors are currently under intense study. Formely

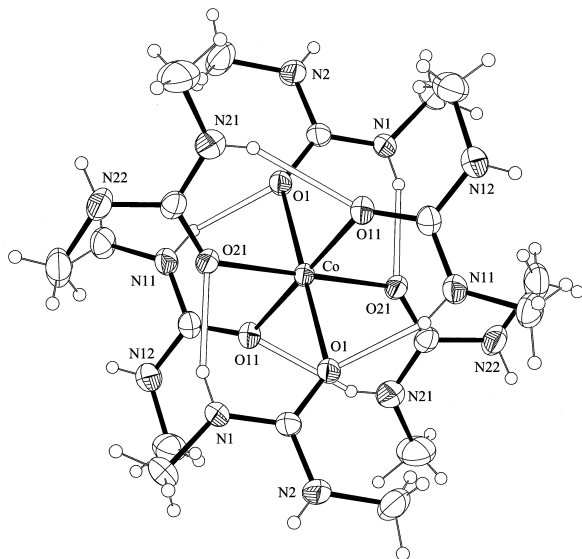


Fig. 3. An ORTEP representation of the cation $[\text{Co}(\text{DMU})_6]^{2+}$ present in the nitrate complex **3**. Open bonds indicate intramolecular (intracationic) hydrogen bonds. An identical labelling scheme is used for atoms generated by symmetry. For clarity, all carbon atoms are not labelled.

considered “unusual” or “nonconventional”, they are now discussed rather frequently in most fields of structural chemistry [1, 6, 45 - 47] and biology [48, 49]. Typical C-H...O(N) separations occur in the 2.2 - 3.0 Å range and the hydrogen bond angle is in the 100 - 180° range [1], while dissociation energies are 0.4 - 4 Kcal mol⁻¹, with the majority < 2 Kcal mol⁻¹ [45]. At the low energy end of the range, the C-H...O hydrogen bond gradually fades into a van der Waals interaction [45]. The high end of the interaction has not yet been well explored; C-H...A bonds stronger than 4 Kcal mol⁻¹ are predicted to occur when very acidic C-H or very basic acceptor groups are involved [45].

The Co-O_{DMU} distances in **1 - 3** are slightly longer compared with those in other cobalt(II) complexes with urea-type ligands [43], because the coordinated oxygen atoms of DMU are involved in hydrogen bonds. All DMU molecules in **1 - 3** are coordinated in a bent fashion, with Co-O-C angles ranging from 126.1(2) to 131.7(2)°. This is the usual way of coordination of urea and its derivatives [50]. Linearly or approximately linearly coordinated ureas have been observed only in few cases [40, 50, 51].

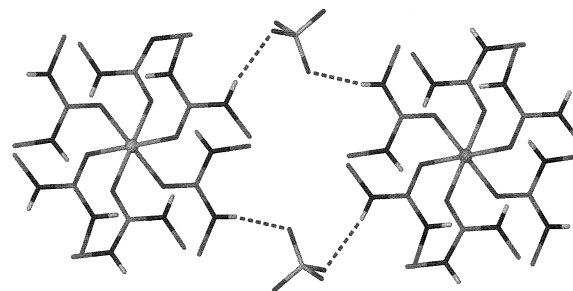


Fig. 4. A view of the 1D network formed by hydrogen bonding between $[\text{Co}(\text{DMU})_6]^{2+}$ cations and ClO_4^- counterions in complex **1**; two cations are shown. Only the intermolecular (interionic) hydrogen bonds are shown.

As it was stated above, we have recently characterized complexes $[\text{M}(\text{DMU})_6](\text{ClO}_4)_2$, where M = Mn, Ni, Zn [24]. These complexes, together with $[\text{Co}(\text{DMU})_6](\text{ClO}_4)_2$ (**1**) described here, constitute an isostructural series. The average M-O_{DMU} bond lengths change according to the sequence Mn^{II} (2.168 Å) > Co^{II} (2.104 Å) > Ni^{II} (2.064 Å) < Zn^{II} (2.095 Å), *i. e.*, they follow the well-known Irving-Williams series [52]. As the thermodynamic stability of the complexes increases from manganese(II) to nickel(II), the coordinative bonds become stronger and the bond lengths decrease in the same order.

Complexes **1 - 3** extend to eleven the number of structurally characterized metal complexes of DMU. The eight, previously structurally characterized, complexes are $[\text{Mn}(\text{NO}_3)_2(\text{DMU})_3]$ [40], $[\text{MnBr}_2(\text{DMU})_3]$ [51], $[\text{Fe}(\text{DMU})_6](\text{ClO}_4)_3$ [53], $[\text{Er}(\text{DMU})_6(\text{H}_2\text{O})](\text{ClO}_4)_3$ [54], $[\text{M}(\text{DMU})_6](\text{ClO}_4)_2$ (M = Mn, Ni, Zn) [24], and $[\text{Cu}(\text{OCIO}_3)_2(\text{DMU})_4]$ [24].

The ClO_4^- and BF_4^- counterions are distorted tetrahedral; for example the O-Cl-O bond angles are in the range 105.3(6) - 114.8(6)°. The sum of angles in the NO_3^- ion is exactly 360° indicating a planar geometry.

We have up to now discussed aspects of the molecular structures of complexes **1 - 3**. Figs. 4 - 6 provide views of the hydrogen bonding networks of the complexes. Distances and angles for the intermolecular (interionic) hydrogen bonds have been included in Tables 2 - 4.

In **1**, two oxygen atoms from each perchlorate, O(2) and O(3), act as hydrogen bond acceptors to NH groups from two DMU ligands belonging to two different $[\text{Co}(\text{DMU})_6]^{2+}$ cations. These ligand-

H Bond	D...A	H...A	D-H...A	Operator of A
N(1)-H(N1)...O(21) ^a	2.887(5)	2.05(4)	162(5)	
N(11)-H(N11)...O(1) ^a	2.902(5)	2.10(4)	156(4)	
N(21)-H(N21)...O(11) ^a	2.935(6)	2.15(5)	161(4)	
C(23)-H(23A)...O(21) ^a	2.731(8)	2.43(7)	103(6)	
N(2)-H(N2)...O(3) ^b	3.033(7)	2.27(4)	167(4)	1 - x, -y, -z
N(12)-H(N12)...O(2) ^b	3.156(8)	2.39(7)	150(6)	1 - x, -1 - y, 1 - z

Table 2. Dimensions of the unique hydrogen bonds (distances in Å and angles in °) for complex 1.

^a Intramolecular (intracationic) hydrogen bonds, see Fig. 2; ^b these oxygen atoms belong to the perchlorate counterions not shown in Fig. 2; A = acceptor; D = donor.

H Bond	D...A	H...A	D-H...A	Operator of A
N(1)-H(N1)...O(21) ^a	2.876(4)	2.12(2)	157(2)	
N(11)-H(N11)...O(1) ^a	2.884(4)	2.09(2)	159(2)	
N(21)-H(N21)...O(11) ^a	2.927(4)	2.14(3)	157(2)	
C(23)-H(23B)...O(21) ^a	2.730(5)	2.38(5)	101(6)	
N(2)-H(N2)...F(2) ^b	2.928(9)	2.24(3)	162(3)	x, 1 + y, -1 + z
N(12)-H(N12)...F(1) ^b	3.114(10)	2.41(4)	150(3)	1 + x, -1 + y, z
N(2)-H(N2)...F(5) ^c	2.994(9)	2.31(3)	161(3)	1 - x, 1 - y, -1 - z
N(12)-H(N12)...F(7) ^c	3.077(10)	2.42(4)	143(3)	1 - x, -y, -z
C(21) ^d -H(21B)...F(3) ^b	3.412(12)	2.54(5)	154(4)	-x, 1 - y, 1 - z

Table 3. Dimensions of the unique hydrogen bonds (distances in Å and angles in °) for complex 2.

^a Intramolecular (intracationic) hydrogen bonds, see Fig. 2; ^b these fluorine atoms belong to the tetrafluoroborate counterions not shown in Fig. 2; ^c disordered fluorine atoms; ^d this atom, which is not labelled in Fig. 2, belongs to the methyl group of a DMU ligand; A = acceptor; D = donor.

H Bond	D...A	H...A	D-H...A	Operator of A
N(1)-H(N1)...O(21) ^a	2.825(3)	2.06(3)	158(3)	-x, -y, -z
N(11)-H(N11)...O(1) ^a	2.861(3)	2.07(3)	158(3)	
N(21)-H(N21)...O(11) ^a	3.036(4)	2.32(4)	154(3)	-x, -y, -z
N(2)-H(N2)...O(33) ^b	3.043(4)	2.33(3)	165(3)	x, y, -1 + z
N(12)-H(N12)...O(32) ^b	3.115(4)	2.41(4)	156(4)	x, -1 + y, z
N(22)-H(N22)...O(32) ^b	3.065(4)	2.41(4)	138(4)	1 - x, -y, -z
C(11) ^c -H(11B)...O(32) ^b	3.443(5)	2.59(4)	154(3)	x, -1 + y, z

Table 4. Dimensions of the unique hydrogen bonds (distances in Å and angles in °) for complex 3.

^a Intramolecular (intracationic) hydrogen bonds, see Fig. 3; ^b these oxygen atoms belong to the nitrate counterions not shown in Fig. 3; ^c this atom, which is not labelled in Fig. 3, belongs to the methyl group of a DMU ligand; A = acceptor; D = donor.

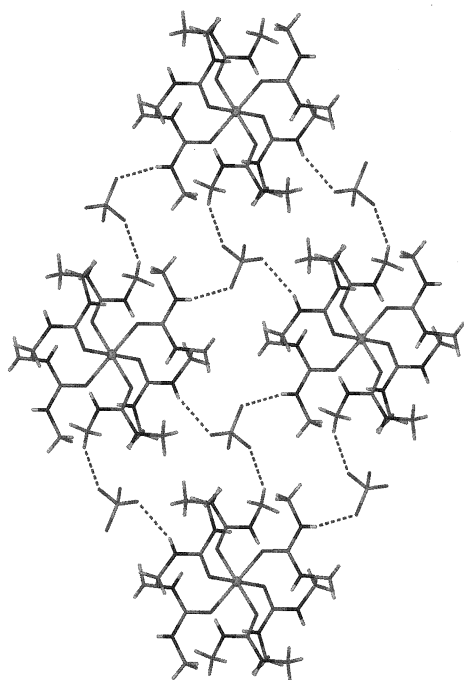


Fig. 5. A view of the 2D network formed by hydrogen bonding between $[\text{Co}(\text{DMU})_6]^{2+}$ cations and BF_4^- counterions in complex 2. Only the intermolecular (interionic) hydrogen bonds are shown. For clarity, the hydrogen bonds to disordered tetrafluoroborate fluorine atoms (see Table 3) have not been drawn.

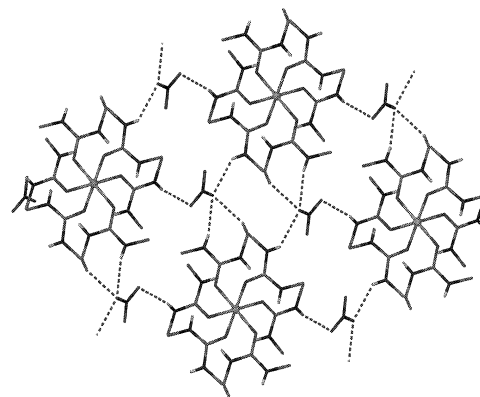


Fig. 6. A view of the 2D network formed by hydrogen bonding between $[\text{Co}(\text{DMU})_6]^{2+}$ cations and NO_3^- counterions in complex 3. Only the intermolecular (interionic) hydrogen bonds are shown.

Table 5. Most characteristic and diagnostic IR fundamentals (cm^{-1}) of free^a DMU and its cobalt(II) complexes **1** - **3**.

DMU	1	2	3	Assignments
~3350 sb	3420 - 3350 sb	3400 - 3270 sb	3395 - 3275 sb	$\nu(\text{NH})$
1628 s	1580 s	1576 s	1576 s	$\nu(\text{CO})$
1591 s	1634 s	1634 s	1635 s	$\nu_{\text{as}}(\text{CN})_{\text{amide}} + \delta_{\text{as}}(\text{NH})$
1541 m	1451 m	1451 m	1456 m	$\delta_{\text{s}}(\text{NH})$
1270 sb	1357 m	1355 m	1355 m	$\delta_{\text{as}}(\text{NH}) + \nu_{\text{as}}(\text{CN})_{\text{amide}}$
1175 m	1183 m	1182 m	1181 m	$\nu_{\text{s}}(\text{N-CH}_3)$
1040 m	1049 m	1043 m	1045 m	$\nu_{\text{as}}(\text{N-CH}_3)$
775 s	767 s	767 s	767 s	$\pi(\text{CO})$
702 w	651 sh	653 sh	648 sh	$\delta(\text{CO})$
508 w	578 m	571 w	570 w	$\delta(\text{NCN})$

^a In its *Cc* crystal phase; b: broad; m: medium; s: strong; sh: shoulder; w: weak.

counterion hydrogen bonds create infinite one-dimensional (1D) assemblies (Fig. 4). As a consequence of the participation of O(2) and O(3) in hydrogen bonding, the Cl-O(2) and Cl-O(3) bond lengths [1.390(5) and 1.366(5) Å, respectively] are slightly longer than Cl-O(4) and Cl-O(5) [1.306(7) and 1.342(6) Å, respectively].

The $[\text{Co}(\text{DMU})_6]^{2+}$ cations of **2** are linked through BF_4^- counterions to generate a 2D network. One dimension is created by two crystallographically independent N-H...F(BF_4) interactions, while the second dimension is achieved through one unique C-H...F(BF_4^-) interaction. Each BF_4^- uses three fluorine atoms as hydrogen bond acceptors to NH groups from the DMU ligands belonging to different cations and to one methyl group of a third cation.

The $[\text{Co}(\text{DMU})_6]^{2+}$ and NO_3^- ions of **3** are arranged in infinite 2D networks through three crystallographically independent intermolecular (interionic) N-H...O(NO_3^-) and one unique C-H...O(32) hydrogen bonds. Each nitrate accepts four hydrogen bonds, one through O(33) and three through O(32).

The intermolecular (interionic) N-H...O, N-H...F hydrogen bonds in the supramolecular structures of **1** and **2** can be regarded as “moderate” [44, 45], though they are weaker than the intramolecular N-H...O(DMU) hydrogen bonds. The intermolecular C-H...F and C-H...O hydrogen bonds present in the crystal structures of **2** and **3**, respectively, are definitely weak [44, 45].

Vibrational spectra of the complexes

The full vibrational analysis of crystalline DMU has been published [39]. Table 5 gives diagnostic IR

bands of the free ligand and its cobalt(II) complexes **1** - **3**. Low-frequency IR (far-IR) and Raman data for **1** - **3** are presented in Table 6. Assignments in Table 5 have been given in comparison with the data obtained for the free, *i. e.* uncoordinated, DMU [39] and its manganese(II) [24, 40], nickel(II) [24], copper(II) [24] and zinc(II) [24] complexes. Low-frequency assignments (Table 6) were assisted by considering the bands of free DMU in the far IR and low-frequency Raman regions, and by studying the variation in band position with changing the counterions (cobalt-ligand bands should appear at approximately the same frequencies) and literature reports [43, 53, 54].

The bands with $\nu(\text{CN})_{\text{amide}}$ character are situated at higher frequencies in the spectra of **1** - **3** than for free DMU, whereas the $\nu(\text{CO})$ bands show a frequency decrease. These shifts are consistent with oxygen coordination, suggesting the presence of $^+\text{N}=\text{C}-\text{O}^-$ resonant forms [51 - 55]. Upon coordination *via* oxygen, the positively charged metal 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, while the double bond character of the CO bond decreases, resulting in an increase of the CN stretching frequency with a decrease in the CO stretching frequency [55].

The IR spectrum of **1** exhibits strong bands at ~1080 and 622 cm^{-1} due to the $\nu_3(\text{F}_2)$ and $\nu_4(\text{F}_2)$ vibrations, respectively, of the uncoordinated ClO_4^- [55]. The broad character and signs of splitting of the band at ~1080 cm^{-1} both indicate the involvement of the ClO_4^- ion in hydrogen bonding; this hydrogen bonding was estab-

Table 6. Cobalt(II)-ligand vibrational frequencies for complexes **1** - **3**.

Complex	$\nu(\text{CoO})$		$\delta(\text{OCO})$	
	IR	Raman	IR	Raman
1	381 m	390 m, 366 m	236 m	221 w
2	381 m	390 w, 363 m	237 m	221 w
3	377 w	389 w, 365 m	240 m	222 w

lished crystallographically (see above). The $\nu_3(\text{F}_2)$ [$\nu_d(\text{BF})$] and $\nu_4(\text{F}_2)$ [$\delta_d(\text{FBF})$] vibrations of the tetrahedral (point group T_d) BF_4^- anion appear at 1100 - 1000 (broad band) and at 535 cm^{-1} , respectively, in the IR spectrum of **2** [55]. The presence of ionic nitrates (point group D_{3h}) in **3**, established crystallographically, also follows from the IR spectrum of this compound through the appearance of the $\nu_3(\text{E}')$ [$\nu_d(\text{NO})$], $\nu_2(\text{A}_2'')$ [$\pi(\text{NO}_3)$] and $\nu_4(\text{E}')$ [$\delta_d(\text{ONO})$] bands at 1385, 833 and 695 cm^{-1} , respectively.

The appearance of one IR-active $\nu(\text{CoO})$ [F_{1u} under O_h] and two Raman-active $\nu(\text{CoO})$ [A_{1g} , E_g under O_h] vibrations in the low-frequency spectra of **1** - **3** reflects their *trans* octahedral stereochemistry [55]. The appearance of only one IR-active $\delta(\text{OCO})$ [F_{1u} under O_h] and one Raman-active $\delta(\text{OCO})$ [F_{2g} under O_h] vibration is also in accord with this stereochemistry.

Concluding Comments and Perspectives

The CoX_2/DMU chemistry ($X = \text{ClO}_4$, BF_4 , NO_3) described in this work has fulfilled its promise as a source of interesting hydrogen bonded networks based on simple metal complexes. It is important to note that complexes **1** and **2** are the only products that have been isolated from the corresponding reaction mixtures in EtOH or MeCN, strongly suggesting that the reactions and crystallizations are selective. The great stability of the $[\text{Co}(\text{DMU})_6]^{2+}$ cation in the solid state can be partly attributed to a *pseudochelate* effect. The “moderate” *intracationic* hydrogen bonds present in the structures of **1** - **3** create six 6-membered *pseudochelating* $\text{CoOCNH}\cdots\text{O}$ rings per Co^{II} atom, giving an extra stabilization to the $[\text{Co}(\text{DMU})_6]^{2+}$ cation. This confirms the general rule (developed for organic compounds [6]) that 6-membered-ring intramolecular hydrogen bonds form in preference to intermolecular hydrogen bonds.

This work has shown that the hexakis(N,N'-dimethylurea)cobalt(II) cation can act as a hydrogen-bonding building block with multi-fold connectivity linking ClO_4^- anions to generate an 1D architecture (**1**), and BF_4^- and NO_3^- anions to yield different 2D hydrogen bonded networks (**2**, **3**). We are presently pursuing our prediction that this cation (and other $[\text{M}(\text{DMU})_6]^{2+}$ cations, see ref. [24]) will form hydrogen bonding contacts to a variety of inorganic and organic anions to generate a rich diversity of networks.

There are two main motifs of intermolecular (interionic) hydrogen bonds that have been observed in the structures of the $\text{Co}^{\text{II}}/\text{DMU}$ complexes. A detailed comparison of the crystal structures of **1** and **2** vs. **3** indicates that the counterion does play a role in the assembly of these complexes. In **1** and **2**, where the anions (ClO_4^- , BF_4^-) are approximately “spherical” and with relatively low coordinating ability [11], two crystallographically unique (*i.e.*, totally four) $\text{N-H}\cdots\text{O}(\text{ClO}_4^-)$ or $\text{F}(\text{BF}_4^-)$ hydrogen bonds form per $[\text{Co}(\text{DMU})_6]^{2+}$ cation, resulting in the formation of 1D (**1**) or 2D (**2**) motifs; the 2D motif in **2** arises from the capability of a fluorine atom to “accept” a hydrogen bond from a methyl group. In other words, each ClO_4^- or BF_4^- anion uses two atoms as hydrogen bond acceptors to NH groups. In **3**, where the counterion (NO_3^-) is more anisotropic with stronger hydrogen-bond acceptors [13], three crystallographically unique (*i.e.*, totally six) $\text{N-H}\cdots\text{O}(\text{NO}_3^-)$ hydrogen bonds form per $[\text{Co}(\text{DMU})_6]^{2+}$ cation, resulting in the formation of a 2D network with a weak $\text{C-H}\cdots\text{O}(\text{NO}_3^-)$ hydrogen bond also contributing to the stabilization of this motif. Each NO_3^- anion also uses (like each ClO_4^- or NO_3^-) two oxygen atoms as hydrogen bond acceptors to NH groups, but one of these atoms, *i.e.*, O(32) “accepts” two hydrogen bonds from NH groups. As a result of the different hydrogen bonding ability of the counterions, in **1** and **2** ten (from a total of twelve) NH groups of each $[\text{Co}(\text{DMU})_6]^{2+}$ building block participate in hydrogen bonds, six of them participating in intramolecular (intracationic) and four in intermolecular (interionic) hydrogen bonds; atom N(22) and its symmetry equivalent are not engaged in hydrogen bonding interactions, see Tables 2, 3 and Fig. 2. On the contrary, in **3** all the twelve NH groups of each $[\text{Co}(\text{DMU})_6]^{2+}$ cation participate in hydrogen bonds (six intramolecular, six intermolecular).

The N-H hydrogens of symmetrical disubstituted ureas prefer to adopt an *anti, anti* (or *trans, trans* [39]) relationship to the carbonyl groups [6, 33], see Fig. 1. Coordination of DMU to cobalt(II) has two consequences. First, while both lone pairs on the carbonyl oxygen atom of free DMU [39, 56] act as hydrogen bond acceptors, in **1-3** one pair acts as a “moderate” [44, 45] hydrogen bond acceptor and the other participates in the formation of the Co-O coordinative bond. Second, the N-H hydrogens of each DMU ligand adopt a *syn, anti* (or *cis, trans*) relationship to the coordinated carbonyl group; the *syn* (or *cis*) configuration of one NH group is necessary for the formation of the 6-membered-ring intramolecular hydrogen bonds, whereas 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 counterions. Thus, the topology of the DMU sheet structure [39, 56] is significantly perturbed by coordination. Based on the above, it appears feasible to control the extent of the perturbation by variation of the nature of the metal ion and the counterion.

The NH groups in the complexes reported here are “moderate” [44, 45] (and not weak) donors because the oxygen atom accepts both a hydrogen and a coordinative bond; thus, the polar resonant forms of the DMU ligands, *i. e.*, $(\text{CH}_3)\text{HN}^+=\text{C}-\text{O}^-$, are stabilized. Since the polarization occurs through π bonds, this effect has been called π -bond cooperativity [44, 45].

We currently work on neutral (and not cationic) metal complexes of DMU using halides as co-ligands to take advantage of the facts that there is more space available for guest molecules and no possibility for unpredictable hydrogen bonding to the counterion. The synthesis of neutral complexes might favour the construction of motifs based on prevailing DMU-DMU interactions. We do believe that N,N'-disubstituted ureas would prove central players in the field of hydrogen bonded networks of coordination complexes.

Experimental Section

All manipulations were performed under aerobic conditions using starting materials (Merck) and solvents as received. Elemental analyses (C, H, N) were conducted by the University of Ioannina, Greece, Microanalytical Service. IR spectra ($4000 - 500 \text{ cm}^{-1}$) were recorded on

a Bruker IFS 113v FT spectrometer with samples prepared as KBr pellets. Far-IR spectra ($500 - 50 \text{ cm}^{-1}$) were recorded on the same Bruker spectrometer using polyethylene pellets. FT Raman data have been collected on a Bruker IFS 66v interferometer equipped with a FRA 106 Raman accessory, a CW Nd-YAG laser source and a liquid-nitrogen Ge detector.

$[\text{Co}(\text{DMU})_6](\text{ClO}_4)_2$ (**1**)

A pink-red solution of $\text{Co}(\text{ClO}_4)_2 \cdot 6 \text{H}_2\text{O}$ (0.73 g, 2.0 mmol) in EtOH (20 ml) and 2,2-dimethoxypropane (DMP, 2.5 ml) was refluxed for 30 min, cooled down to room temperature and then treated with solid DMU (1.29 g, 14.6 mmol). No noticeable colour change occurred. The reaction flask was stored at 4 °C for 3 d and the obtained pink microcrystalline solid was collected by filtration, washed with Et₂O ($2 \times 5 \text{ ml}$) and dried *in vacuo* over P₄O₁₀. The yield was ~55%. Crystals suitable for single-crystal X-ray crystallography were obtained by diluting the original solution with more EtOH (15 ml) and layering it with Et₂O / n-hexane (1:1 v/v, 40 ml). – C₁₈H₄₈N₁₂O₁₄Cl₂Co (786.51): calcd. C 27.48, H 6.16, N 21.37; found C 27.80, H 6.06, N 21.12. *Caution!* Perchlorate salts are potentially explosive. Although no detonation tendencies have been observed in our experiments, caution is advised and handling of only small quantities is recommended.

$[\text{Co}(\text{DMU})_6](\text{BF}_4)_2$ (**2**)

A pink solution of $\text{Co}(\text{BF}_4)_2 \cdot 6 \text{H}_2\text{O}$ (0.68 g, 2.0 mmol) in EtOH (30 ml) and DMP (2.5 ml) was refluxed for 20 min, cooled to ~35 °C and then treated with solid DMU (1.20 g, 13.6 mmol). No noticeable colour change occurred. The reaction mixture was refluxed for a further 15 min, cooled to room temperature and layered with Et₂O (35 ml). Slow mixing gave pink crystals suitable for X-ray crystallography, which were collected by filtration, washed with cold EtOH (2 ml) and copious amounts of Et₂O, and dried *in vacuo* over P₄O₁₀. Typical yields were in the 75 - 83% range. – C₁₈H₄₈N₁₂O₆B₂F₈Co (761.23): calcd. C 28.40, H 6.37, N 22.08; found C 28.56, H 6.29, N 21.78.

$[\text{Co}(\text{DMU})_6](\text{NO}_3)_2$ (**3**)

A pink-red solution of $\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ (0.58 g, 2.0 mmol) in Me₂CO (22 ml) and DMP (2.5 ml) was refluxed for 15 min and treated, while hot, with solid DMU (1.29 g, 14.6 mmol). DMU soon dissolved to give a homogeneous solution of the same colour, which was further refluxed for 20 min. After cooling to room temperature, the solution was layered with Et₂O (20 ml).

Table 7. Summary of crystal data, data collection and structure refinement for X-ray diffraction studies of complexes **1**, **2** and **3**.

Compound	1	2	3
Chemical formula	C ₁₈ H ₄₈ N ₁₂ O ₁₄ Cl ₂ Co	C ₁₈ H ₄₈ N ₁₂ O ₆ F ₈ B ₂ Co	C ₁₈ H ₄₈ N ₁₄ O ₁₂ Co
Formula weight	786.51	761.23	711.61
Colour, habit	pink prisms	pink prisms	pink plates
Crystal system	triclinic	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	8.058(8)	7.993(8)	7.858(3)
<i>b</i> (Å)	10.71(1)	10.67(1)	10.742(4)
<i>c</i> (Å)	11.69(1)	11.62(1)	11.089(4)
α (°)	68.53(3)	67.88(3)	67.92(1)
β (°)	81.21(4)	80.67(3)	82.45(1)
γ (°)	81.32(3)	81.86(3)	81.74(1)
<i>V</i> (Å ³)	924(1)	902.3(2)	855.3(6)
<i>Z</i>	1	1	1
<i>D</i> _{calc} (g cm ⁻³)	1.413	1.401	1.382
μ (mm ⁻¹)	0.681	0.565	0.574
<i>F</i> (000)	413	397	377
Radiation (Å)	Mo- <i>K</i> α ($\lambda = 0.71073$)	Mo- <i>K</i> α ($\lambda = 0.71073$)	Mo- <i>K</i> α ($\lambda = 0.71073$)
Temperature (K)	298	298	298
Scan mode/speed (° min ⁻¹)	θ -2 θ /2.3	θ -2 θ /3.5	θ -2 θ /2.0
θ Range (°)	1.9 - 24.0	1.9 - 25.0	2.0 - 25.0
<i>h, k, l</i> Ranges	-9 \rightarrow 0, -12 \rightarrow 12, -13 \rightarrow 13	0 \rightarrow 9, -12 \rightarrow 12, -13 \rightarrow 13	-9 \rightarrow 9, -12 \rightarrow 0, -13 \rightarrow 12
Measured reflections	3148	3442	3184
Unique reflections	2909 (<i>R</i> _{int} = 0.0094)	3192 (<i>R</i> _{int} = 0.0065)	3007 (<i>R</i> _{int} = 0.0228)
Reflections used [<i>I</i> > 2 σ (<i>I</i>)]	2533	2959	2632
<i>w</i> ^a	<i>a</i> = 0.0647; <i>b</i> = 1.0037	<i>a</i> = 0.0512; <i>b</i> = 0.1958	<i>a</i> = 0.0420; <i>b</i> = 0.3060
GoF (on <i>F</i> ²)	1.051	1.059	1.098
<i>R</i> 1 ^b [<i>I</i> > 2 σ (<i>I</i>)]	0.0522	0.0342	0.0392
<i>wR</i> 2 ^c [<i>I</i> > 2 σ (<i>I</i>)]	0.1357	0.0974	0.0978
($\Delta\rho$) _{max} /($\Delta\rho$) _{min} (e Å ⁻³)	0.538/-0.437	0.400/-0.170	0.316/-0.300

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

^c $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Slow mixing gave well-formed, X-ray-quality pink crystals, which were collected by filtration, washed with copious amounts of Et₂O and dried *in vacuo* over silica gel. The yield was ~70%. The product appears slightly hygroscopic. – C₁₈H₄₈N₁₄O₁₂Co (711.61): calcd. C 30.38, H 6.81, N 27.56; found C 30.62, H 6.99, N 27.87.

The above preparations are representative. Complexes **1** - **3** can be isolated using a variety of solvents and DMU:Co^{II} ratios, see “Synthetic comments” above.

Crystal structure determinations

Pink prismatic crystals of **1** (0.10 × 0.35 × 0.60 mm), **2** (0.10 × 0.15 × 0.40 mm) and **3** (0.20 × 0.45 × 0.50 mm) were mounted in air. Diffraction measurements were made on a Crystal Logic Dual Goniometer diffractometer using graphite monochromated Mo-*K* α radiation. Crystal data and full details of the data collection and data

processing are listed in Table 7. Unit cell dimensions were determined and refined by using the angular settings of 25 automatically centred 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 **3**) absorption corrections were applied using Crystal Logic software.

The structures were solved by direct methods using SHELXLS-86 [57] and refined by full-matrix least-squares techniques on *F*² with SHELX-93 [58]. For all three structures, all non-H atoms were refined using anisotropic thermal parameters, except tetrafluoroborate fluorine atoms F(1), F(2), F(3) and F(4) of **2** which were found disordered and refined anisotropically in two orientations with occupation factors free to vary. All H atoms of **1** - **3**, except those on C(13) and C(23) in **2** which were introduced in calculated positions as riding

on bonded atoms, were located by difference maps and refined isotropically. Three X-ray crystallographic files for complexes **1** - **3**, in CIF format, have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, under the numbers 188969 (**1**), 188970 (**2**) and 188971 (**3**). Copies may

be requested free of charge from the Director of CCDC (E-mail: deposit@ccdc.cam.ac.uk).

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