Research Article

Synthesis, X-Ray Structure, and Characterization of a Complex Containing the Hexakis(urea)cobalt(II) Cation and Lattice Urea Molecules

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Received 28 August 2007; Accepted 10 November 2007

Recommended by Osamu Yamauchi

The 12 : 1 reaction of urea (U) with CoI₂ in EtOH yielded the “clathrate-coordination” compound [CoU₆]I₂ · 4U (1). The complex crystallizes in the monoclinic space group P2₁/c. The lattice constants are \( a = 9.844(4), \) \( b = 7.268(3), \) \( c = 24.12(1) \) Å, and \( \beta = 98.12(1) \)°. The crystal structure determination demonstrates the existence of octahedral [CoU₆]²⁺ cations, I⁻ counterions, and two different types (two U₁ and two U₂) of hydrogen-bonded, lattice urea molecules. The [CoU₆]²⁺ cations and the U₁ lattice molecules form two-dimensional hydrogen-bonded layers which are parallel to the 〈ab〉 plane. The I⁻ anions are placed above and below each layer, and are hydrogen bonded both to U₁ molecules and [CoU₆]²⁺ cations. Each U₂ molecule is connected to a [CoU₆]²⁺ cation through an N–H···O hydrogen bond resulting in a three-dimensional network. Room temperature magnetic susceptibility and spectroscopic (solid-state UV/Vis, IR, Raman) data of 1 are discussed in terms of the nature of bonding and the known structure.

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1. INTRODUCTION

Urea, \( \text{H}_2\text{NCONH}_2 \) (hereafter abbreviated as U), is a very old compound, first isolated by Rouelle in 1773 and subsequently synthesized from inorganic materials by Wöhler in 1828. There is a renewed interest in the coordination chemistry of U and its substituted derivatives. These efforts are driven by a number of considerations, including the solution of pure chemical [1] and spectroscopic [2] problems, the desire to provide useful bioinorganic models for the intermediates in the catalytic mechanism of the metalloenzyme urease (for its active site see Scheme 1) [3, 4], and the goal to isolate functional complexes with interesting supramolecular structures [5]. Single-crystal X-ray crystallography has revealed [6] that U normally coordinates as a monodentate ligand through the oxygen atom (I in Scheme 2). In a very limited number of cases [7, 8], U behaves as an N,O-bidentate bridging ligand (II in Scheme 2), while in [Hg₂Cl₄U₂] each U molecule bridges the two Hg²⁺ atoms through only the oxygen atom [9] (III in Scheme 2). Of particular chemical/biological interest is the ability of U to undergo metal-promoted deprotonation [3, 10]; the monoanionic ligand \( \text{H}_2\text{NCONH}^- \) adopts the \( \mu_2 \) (IV in Scheme 2) and \( \mu_3 \) (V in Scheme 2) coordination modes.

Free ureas have been among the central players in organic crystal engineering [11]. In contrast, little is known about the supramolecular architectures created by hydrogen bonding interactions between simple metal-urea complexes. By reacting metal ions with ureas that contain both an efficient coordination site and two hydrogen bonding functionalities, assembly can be dictated by intermolecular/interinorganic hydrogen bonding interactions. We have relatively recently [12–14] embarked on a program which has as a short-term goal the creation of supramolecular structures based on hydrogen bonding interactions between simple metal complexes with U or substituted ureas as ligands. Literature [5] reveals the existence of single-crystal X-ray and neutron structures for the impressive complex [CoU₆]Br₂ · 4U, which has been
performed with a Carlo Erba EA 108 analyzer, [CoU₆]I₂·4U (hereafter referred to as 1).

To a stirred refluxing colorless solution of U (0.72 g, 12 mmol) in EtOH (30 cm³) was added solid CoI₂ (0.31 g, 1.0 mmol) in small portions. The obtained blue solution was refluxed for further 15 minutes. A noticeable color change to pink occurred after cooling down. The solution began to deposit X-ray quality, orange crystals of 1 after 24 hours. When precipitation was judged to be complete, the product was collected by filtration, washed with a little cold EtOH (1·2 cm³) and Et₂O (2·5 cm³), and dried in air. The yield was 77% (based on the metal); found %: C, 13.22; H, 4.50; N, 30.48. Calc % for C₁₀H₄₀N₂₀O₁₀CoI₂: C, 13.15; H, 4.42; N, 30.68; selected IR data (KBr, cm⁻¹): 3450 (sh), 3438 (s), 3346 (m), 3438 (sh), 1685 (sh), 1666 (s), 1648 (sh), 1622 (m), 1578 (m), 1478 (m), 1444 (m), 1156 (m), 1050 (w), 780 (m), 617 (sh), 600 (w), 570 (m), 532 (m), 366 (m).

2. EXPERIMENTS

All manipulations were performed under aerobic conditions using materials and solvents as received. IR spectra were recorded on a Perkin-Elmer PC16 FT-IR spectrometer with samples prepared as KBr pellets. Far-IR spectra were recorded on a Bruker IFS 113v FT spectrometer with samples prepared as polyethylene pellets. Solid-state (diffuse reflectance, DRS) electronic spectra in the 350–850 nm range were recorded on a Varian Cary 3 spectrometer equipped with an integration sphere. Room temperature magnetic susceptibility measurements were carried out by Faraday's method using a Cahn-Ventron RM-2 balance standardized using Pascal’s constants. C, H and N elemental analyses were described as a “clathrate-coordination” compound. We were interested in investigating whether a similar iodide complex could exist; the present paper provides the answer to this question. Another goal of this work has been the study of the vibrational spectra of metal ion-U complexes, especially in view of the reassignment of the vibrational spectrum of free U [15].

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2.1. X-ray crystallography

X-ray data were collected at 298 K using a Crystal Logic Dual Goniometer diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Lorentz, polarization, and Ψ-scan absorption corrections were applied using Crystal Logic software. Symmetry equivalent data were averaged with Rint = 0.0202, to give 3006 independent reflections from a total 3086 collected. The structure was solved by direct methods and refined by full-matrix least-squares on F², using 3006 reflections and refining 276 parameters. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms bonded to nitrogen atoms were located by difference maps and their positions were refined isotropically. There were no significant residual peaks in the electron density map. Details of the data collection and refinement are given in Table 1. Topological analysis of the nets was performed using TOPOS program package [16, 17].

3. RESULTS AND DISCUSSION

3.1. Synthetic comments

The CoI₂/U reaction system was synthetically investigated in the past. Depending on the reaction and crystallization conditions, the complexes [CoU₆]I₂ [18], [CoU₆]I₃·2U [19], [CoU₂(H₂O)₄]I₃·2U [20] and [CoU₄(H₂O)₂]I₂ [20] were isolated and structurally characterized. In these four complexes, the U : CoII ratio varies from 1 : 1 to 8 : 1. We wondered if complexes with a higher U to CoII ratio, that is, a higher urea percentage, would be capable of existence. Thus, the 12 : 1 reaction of U and CoI₂ in refluxing EtOH gave orange crystals of compound [CoU₆]I₂·4U (1) in very good yield (ca. 80%). The reaction can be represented by the stoichiometric equation (1):

\[
\text{CoI}_2 + 10 \text{U} \xrightarrow{\text{EtOH}} [\text{CoU}_6]_2 \cdot 4\text{U}. \tag{1}
\]

The “wrong” stoichiometry employed, that is, U : CoI₂ = 12 : 1 instead of 10 : 1 (required by (1)), is necessary for the precipitation of pure 1. The 10 : 1 reaction ratio in EtOH under reflux leads to a mixture of 1 and [CoU₆]I₃·2U [19];
the identity of the latter was confirmed by unit cell determination. The same complex cannot be prepared in other solvents; use of MeCN leads to complexes [CoU2(H2O)4][CoI4] (2) which has yet to be structurally characterized.

3.2. Description of structure

The structure of 1 consists of octahedral [CoU6]2+ cations, I− anions and lattice urea molecules (four lattice urea molecules per cation). The structure of the [CoU6]2+ cation is shown in Figure 1, and selected bond lengths and angles are listed in Table 2. The CoII ion sits on an inversion centre and is surrounded by six O-bonded urea ligands. The octahedral coordination around the CoII atom is slightly distorted, as evidenced by the Co–O bond distances and O–Co–O bond angles. The Co–O bond distances in the title complex are comparable to those in other [CoU6]2+ complexes [18–20]. The urea molecules are hydrogen-bonded both to U1 molecules and [CoU6]2+ cations. Each U1 molecule accepts five hydrogen bonds connecting two [CoU6]2+ cations. The I− anions are placed above and below each layer and are hydrogen bonded to the U1 molecules. Each I− anion accepts two hydrogen bonds from U1 molecules and [CoU6]2+ cations. The asymmetric unit of 1 contains five crystallographically independent urea molecules (U1 and U2, resp.). The crystal structure of 1 have been included in Table 3. The asymmetric unit of 1 contains five crystallographically independent urea molecules; three of them are coordinated to the CoII atom while the other two (hereafter termed U1 and U2) are lattice molecules. The [CoU6]2+ cations and the U1 lattice molecules form two-dimensional (2D) hydrogen-bonded layers which are parallel to the ab plane and separated by about 12 Å along the c axis (Figure 2).

| Table 1: Crystal data and structure refinement for 1. | Table 2: Selected bond lengths (Å) and angles (°) for 1; symmetry transformation used to generate equivalent atoms: a 1−x, −y, −z; atoms C(32), O(31), N(31), N(32) and C(42), O(41), N(41), N(42) belong to the two crystallographically independent lattice U molecules (U1 and U2, resp.). |
|------------------------------------------------------|----------------------------------------------------------|
| **Empirical formula** | Co10H40CoI2N20O10                                         |
| **Formula weight** | 913.35                                                   |
| **Crystal size** | 0.10 × 0.20 × 0.50                                        |
| **Crystal system** | Monoclinic                                                |
| **Space group** | P21/c                                                     |
| **θ range for data collection** | 1.71 ≤ θ ≤ 24.97                                         |
| **a, Å** | 9.844(4)                                                 |
| **b, Å** | 7.268(3)                                                 |
| **c, Å** | 24.12(1)                                                 |
| **α, °** | 90                                                        |
| **β, °** | 90                                                        |
| **γ, °** | 90                                                        |
| **V, Å³** | 1708(1)                                                  |
| **ρ, g·cm⁻³** | 1.775                                                     |
| **µ, mm⁻¹** | 2.380                                                     |
| **GOF** | 1.057                                                     |
| **R1** | 0.027                                                     |
| **wr2** | 0.066                                                     |

*If I > 2σ(I).
The symmetry-equivalent atoms are not labeled.

The U₂ molecules are hydrogen bonded to each other through the N(41)–H(41A)···O(41)f and N(42)–H(42A)···O(41)g hydrogen bonds to form one dimensional tapes that run parallel to the b axis. The U₂ tapes are parallel to the "[CoU₆]I₂·2U₁" layers and are separated by 9.844 Å along the a axis. Each U₂ molecule is connected to a [CoU₆]²⁺ cation through the N(2)–H(2A)···O(41)c hydrogen bond (Figure 3) resulting in a three-dimensional (3D) hydrogen-bonded network; the U₂ tapes are placed within the "[CoU₆]I₂·2U₁" layers and connect them to the third dimension.

From the topological point of view, the [CoU₆]²⁺ cations and the U₁ molecules form a 2D framework, with a (4,4) topology and two different types of 4-connected nodes. Each [CoU₆]²⁺ serves as a 4-connected node within the 2D net where the other type of 4-connected node is situated on the centre of the R₂(8) ring formed by two [CoU₆]²⁺ and two U₁ molecules (Figure 2). The "[CoU₆]²⁺·2U₁" layers are connected to the third dimension only through the [CoU₆]²⁺ cations, which therefore serve as 6-connected nodes within the 3D framework. Each U₂ molecule is hydrogen bonded to two other U₂ molecules and at the same time to one [CoU₆]²⁺. In this arrangement, each U₂ molecule serves as a 3-connected node within the 3D framework. Therefore, the 3D framework is a trinodal net with 3-, 4-, and 6-connected nodes and a unique (6₃)₂(4₁-4₆)(4₄-6¹₀·8) topology (Figure 4(a)). If we consider that the U₂ molecules simply connect the 2D layers and merge them to the [CoU₆]²⁺ nodes, then we can simplify the 3D framework to a binodal net with 4- and 8-connected nodes and a unique (4¹-6²)(4₁⁶-6¹₂) topology (Figure 4(b)). The latter network can be simplified further to a uninodal net by merging the 4-connected nodes to the 8-connected nodes resulting in a 12-connected network with a unique 3¹₈·4¹₄·5⁴ topology (Figure 4(c)). Interestingly, the new 12-connected network has the same coordination sequence with the fccu net [21].
Complex 1 joins a handful of structurally characterized complexes containing the octahedral cation [CoU₆]^{2+} [5, 18, 19, 22]; it is isostructural with [CoU₆]Br₂·4U [5] and [NiU₆]I₂·4U [23].

### 3.3. Physical and spectroscopic characterization

The room temperature value of the effective magnetic moment (μₑff) for 1 is 4.93 BM per metal ion, to be compared with the spin-only (g = 2) μₑff value of 3.87 BM. This value is within the range observed for six-coordinate, high-spin cobalt(II) complexes [24]. Because of the intrinsic orbital angular momentum in the octahedral ground state 4T₁g(F), there is consistently a considerable orbital contribution and μₑff values for such compounds around room temperature are between 4.7 and 5.2 BM.

The solid-state electronic spectral data of 1 also indicate an octahedral stereochemistry around cobalt(II). A multiple structured bond, assigned to 4T₁g(F) → 4T₁g(P), is seen in the visible region near 530 nm with a clear shoulder at 474 nm [25]. The multiple structure arises from the admixture of spin forbidden transitions to doublet states mainly derived from 2G and 2H. The 4T₁g(F) → 4A₂g transition appears as an ill-defined shoulder at ~665 nm [25]. The calculated ligand field parameters from the two transitions in the visible region are 10Dq = 8050 cm⁻¹ and B = 865 cm⁻¹ [25]; these values are typical for a Co^{II}O₆ chromophore.

The full vibrational analysis of crystalline U has been published [15]. Table 4 gives diagnostic IR bands of the free ligand and 1. Assignments have been given in comparison with the data obtained for the free, that is, uncoordinated, U [15] and its manganese(II) complexes [2]. The bands with ν(CN) character are situated at higher wavenumbers in the spectrum of 1 than for free U, whereas the ν(CO) band shows a frequency decrease. These shifts are consistent with oxygen coordination, suggesting the presence of N=C–O resonant forms [15], see Scheme 3. 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 simultaneous decrease in the CO stretching frequency [2, 12–14]. The appearance of two bands for each of the δₐₕ(NH₂) and δₛ(NH₂) modes in 1 may indicate the existence of two types of U molecules, coordinated and uncoordinated (lattice). However, the appearance of one band for each of the other modes suggests that the coordinated

![Figure 4: Views of (a) the trinodal 3D network, (b) the simplified binodal network, and (c) the simplified uninodal 12-connected network of 1.](image)
and lattice (but hydrogen bonded) U molecules of I cannot, in general, be differentiated in the vibrational spectrum. This is not unexpected, bearing in mind that the hydrogen bonds have an effect similar to that of coordination on the shifts of the CO and CN stretching vibrations. This can be explained [15] by regarding the hydrogen bond as a donor-acceptor “complex,” with the oxygen atom as the donor and the hydrogen atom as the acceptor. The appearance of one IR-active ν(CO) vibration at 366 cm$^{-1}$ ($F_{\text{ua}}$ under $O_{h}$) in the low-frequency region of I reflects the trans octahedral stereochemistry of [CoU$_{6}$]$^{2+}$ [13, 26].

4. CONCLUSIONS

This work has shown that the hexakis(urea)cobalt(II) cation can act as a hydrogen bonding building block with multi-fold connectivity linking I$^{−}$ anions and U molecules to generate a 3D architecture. We are presently pursuing our prediction that this cation will form hydrogen bonding contacts to a variety of inorganic and organic anions to generate a rich diversity of networks. Complex I, which is isostructural with its bromide analogue [5], is becoming the fifth structurally characterized member of the Co$^{II}$/I$^{−}$/U family of complexes [18–20], emphasizing the rich molecular and supramolecular chemistry of this system.

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. Alternatively, the metal ion may exert an electronic effect on the individual proton and acceptor sites, and influence hydrogen bonding in a more subtle manner. The latter effect lets us believe that the reactions of other metal ions with urea may lead to the formation of complexes with novel supramolecular structures.

ACKNOWLEDGMENTS

The authors thank Professor H. O. Desseyn (University of Antwerp, Belgium) for providing them with the far-IR spectrum of I, and for helpful discussions. They also thank Professor Vladislav Blatov (Samara State University, Russia) and Professor Michael O’Keeffe (Arizona State University, USA) for helpful discussions on the topological analysis of the nets. G.S. Papaefstathiou thanks the Special Account for Research Grants (SARG) of the National and Kapodistrian University of Athens for funding this work.

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| Assignment | U | I |
|------------|---|---|
| $v_{\text{ua}}$(NH$_2$) | 3450, 3444 | 3446, 3438 |
| $v_{\text{ua}}$(NH$_2$) | 3349, 3341 | 3346, 3335 |
| $\delta$(NH$_2$) | 1683 | 1685, 1666 |
| $\delta$(NH$_2$) | 1625 | 1648, 1622 |
| $v$(CO) | 1601 | 1578 |
| $v_{\text{ua}}$(CN) | 1466 | 1478 |
| $v$(CN) | 1003 | 1018 |
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