A Novel One-Dimensional Copper Mellitate Complex Featured by $\text{Cu}(\text{H}_2\text{O})_2(\text{urea})[\text{C}_6(\text{COO})_4(\text{COOH})_2]_{n/2n}$ - Polyanions

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HAL Id: hal-02867543

<https://hal.science/hal-02867543>

Submitted on 14 Jun 2020

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A Novel One-Dimensional Copper Mellitate Complex Featured by $\{\text{Cu}(\text{H}_2\text{O})_2(\text{urea})[\text{C}_6(\text{COO})_4(\text{COOH})_2]\}_n^{2n-}$ Polyanions

Roberto Köferstein^[a,b] and Christian Robl^{*[a]}

*Corresponding Author

[a] Institute of Inorganic and Analytical Chemistry, Friedrich-Schiller-University Jena,
Humboldtstrasse 8, 07743 Jena, Germany

[b] Institute of Chemistry, Inorganic Chemistry, Martin Luther University Halle-Wittenberg,
Kurt-Mothes-Strasse 2, 06120 Halle, Germany

Abstract. Blue monoclinic single crystals of the novel one-dimensional $[\text{H}_3\text{N}-(\text{CH}_2)_6-\text{NH}_3][\text{Cu}(\text{H}_2\text{O})_2(\text{urea})(\mu_2-\text{C}_6(\text{COO})_4(\text{COOH})_2)]\cdot\text{H}_2\text{O}$ coordination polymer have been prepared in aqueous solution at room temperature in the presence of 1,6-diaminohexane and urea. Space group $P2_1/n$ (no. 14) with $a = 958.48(9)$, $b = 1465.74(11)$, $c = 1821.14(12)$ pm, $\beta = 97.655(8)^\circ$. The Cu^{2+} cation is coordinated in a square pyramidal manner by two oxygen atoms stemming from the dihydrogen mellitate tetraanion, one oxygen atom from the urea molecule, and two water molecules. The Cu–O distances are between 193.3(2) and 229.4(2) pm. The connection between Cu^{2+} and $[\text{C}_6(\text{COO})_4(\text{COOH})_2]^{4-}$

yields infinite chain-like polyanions parallel to $[\bar{1}01]$ with a composition of $\{\text{Cu}(\text{H}_2\text{O})_2(\text{urea})[\text{C}_6(\text{COO})_4(\text{COOH})_2]\}_n^{2n-}$. The dihydrogen mellitate tetraanion adopts a μ_2 coordination mode. The $[(\text{H}_3\text{N}-(\text{CH}_2)_6-\text{NH}_3)]^{2+}$ cations are accommodated between the chains as counter cations. The hexane-1,6-diammonium cations adopt a partial *synclinal* conformation. The chains are connected by strong and weak hydrogen bonds. Magnetic measurements reveal a paramagnetic Curie-Weiss behaviour and a magnetic moment of $1.93 \mu_B$ per Cu^{2+} . Thermoanalytical investigations in air show that the complex is stable up to 135°C . Following decomposition processes yielding CuO .

Introduction

The connection between metal cations and multi-dentate complexing agents, like the anions of benzenecarboxylic acids leads to coordination polymers with various structural features and interesting properties [1–8]. The carboxylate groups of benzenecarboxylic acids anions are able to coordinate metal ions in flexible modes. For example, the connection between the anions of benzenehexacarboxylic acid (mellitic acid) and metal cations results in coordination polymers with chain- and layer-like structures as well as in three-dimensional frameworks (so-called MOF's) [9–22]. Besides of the fully deprotonated form, complexes with mono-, di-, tri-, and tetra-protonated anions of benzenehexacarboxylic acid are known [23–31]. The structures of such coordination polymers can be varied using rational design synthesis e.g. additional N- or O-donor ligands and organic amines as template molecules, respectively [28,32–42]. The obtained crystal structures also depend on the reaction conditions. Previous works show that e.g. the reaction between Cu^{2+} and benzenehexacarboxylic acid results either in a two-dimensional layer-like structure [20,26,27] or in a three-dimensional framework [21,43]. Moreover, transition metal benzene carboxylato complexes show interesting magnetic properties [12,22,26,44–48] and they are suitable as catalysts for e.g. oxidation, reduction, and isomerisation reactions [49–53].

Herein, we report on a novel one-dimensional copper dihydrogen mellitate complex with urea as additional O-donor ligand and 1,6-diaminohexane as template molecule.

Results and Discussion

The Cu^{2+} cations in $[\text{H}_3\text{N}-(\text{CH}_2)_6-\text{NH}_3][\text{Cu}(\text{H}_2\text{O})_2(\text{urea})(\mu_2-\text{C}_6(\text{COO})_4(\text{COOH})_2)]\cdot\text{H}_2\text{O}$ are five-coordinated in a distorted square pyramidal fashion (Fig. 1). The equatorial positions are formed by two carboxylate oxygen atoms (O(1), O(8)) stemming from two different, but crystallographically equivalent, dihydrogen mellitate tetraanions, one carbonyl oxygen atom from the urea molecule (O13)) and one water molecule (O(w2)) with Cu–O distances between 193.3(2) and 200.2(2) pm. The apical position is occupied by the water molecule O(w3) with a larger bond length of 229.4(2) pm (Tab. 1). The best least-square-plane through Cu, O(8), O(13), O(1) and O(w2) shows an average deviation of 14.5 pm. The angles between the equatorial atoms are close to the expected values of 90° and 180° . Coordination number five could also be described by a distorted trigonal bipyramid. In that case, the equatorial plane is formed by O(w3), O(w2), and O(13) and the average deviation from a best plane is only 2.5 pm. However, the angles between the atoms in the equatorial plane deviate considerably from 60° and 120° and the

distances between the ligand atoms differ over a wide range. In contrast to *Diniz et al.* [54] a smaller deviation from the least-square-plane fitted to the equatorial atoms is not a sufficient criterion for the type of the polyhedron. More important is the comparison of angles and distances between the ligand atoms. Hence, the coordination polyhedron around Cu^{2+} is best described by a distorted square pyramid. Employing the method of *Trömel* [55] the bond order of 2.01 is very close to the expected value.

Figure 1. The coordination environment of Cu^{2+} (Ellipsoids are given at 50% probability, arbitrary radii for hydrogen atoms).

Table 1. The Coordination Environment of Cu^{2+}

bond lengths (pm)			
Cu–O(8)	193.3(2)	Cu–O(w2)	200.2(2)
Cu–O(13)	196.5(2)	Cu–O(w3)	229.4(2)
Cu–O(1)	194.9(2)		
bond angles (°)			
O(8)–Cu–O(1)	177.32(8)	O(1)–Cu–O(13)	90.58(8)
O(8)–Cu–O(13)	87.28(8)	O(1)–Cu–O(w2)	94.47(8)
O(8)–Cu–O(w2)	88.04(8)	O(1)–Cu–O(w3)	89.32(8)
O(8)–Cu–O(w3)	89.69(8)	O(13)–Cu–O(w3)	105.16(8)
O(w2)–Cu–O(w3)	91.59(9)	O(13)–Cu–O(w2)	162.57(9)

The dihydrogen mellitate tetraanion (dihydrogen benzenehexacarboxylate tetraanion) (Fig. 2) is approximately planar with respect to the carbon skeleton. The largest deviation from a plane fitted to the carbon atoms is 17.4 pm (C(9)). The carboxylate groups are twisted against the C_6 -ring by 46.7° (C(7), O(1), O(2)), 60.1° (C(8), O(3), O(4)), 50.2° (C(9), O(5), O(6)), 113.8° (C(10), O(7), O(8)), 44.5° (C(11), O(9), O(10)), and 64.8° (C(12), O(11), O(12)), respectively. The C–O bond lengths of the deprotonated carboxylate groups range from 123.1(3) to 127.1(3) pm. On the other hand the C–O bonds of the COOH groups, which are in the meta position, are between 121.7(3) and 129.8(3) pm (Tab. 2). COOH groups in meta position are also found in calcium dihydrogen mellitate [29], whereas in e. g. copper-, cobalt- and nickel dihydrogen mellitates with N-donor ligands the carboxylic groups are in para position [28,30,34,45]. The urea molecule is planar and can be described by the point group C_s in good approximation. The C–O bond length is 126.1(3) pm and the C–N distances are 132.2(4) and 134.3(4) pm (Tab. 2). In spite of the coordination to Cu^{2+} the C–O bond length does not significantly differ from the one found in the uncoordinated urea molecule [56,57].

Figure 2. The dihydrogen mellitate tetraanion (Ellipsoids are given at 50% probability, arbitrary radii for hydrogen atoms).

Table 2. Bond Lengths (pm) of the Dihydrogen Mellitate Tetraanion, the Urea Molecule and the Hexane-1,6-diammonium Cation

Dihydrogen Mellitate Tetraanion					
C(1)–C(2)	139.3(3)	C(4)–C(10)	151.0(3)	C(10)–O(7)	124.6(3)
C(1)–C(6)	140.7(3)	C(5)–C(11)	151.4(3)	C(10)–O(8)	125.8(3)
C(2)–C(3)	140.0(3)	C(6)–C(12)	152.1(3)	C(11)–O(9)	121.8(3)
C(3)–C(4)	139.9(3)	C(7)–O(1)	127.1(3)	C(11)–O(10)	129.0(3)
C(4)–C(5)	139.4(3)	C(7)–O(2)	123.1(3)	C(12)–O(11)	124.5(3)
C(5)–C(6)	139.6(3)	C(8)–O(3)	126.8(3)	C(12)–O(12)	125.9(3)
C(1)–C(7)	151.9(3)	C(8)–O(4)	124.1(3)	O(6)–H(19)	102(4)
C(2)–C(8)	151.7(3)	C(9)–O(5)	121.7(3)	O(10)–H(20)	76(4)
C(3)–C(9)	150.9(3)	C(9)–O(6)	129.8(3)		
Urea					
O(13)–C(13)	126.1(3)	N(3)–H(27)	91(4)	N(4)–H(30)	82(4)
C(13)–N(4)	132.2(4)	N(3)–H(28)	80(4)	N(4)–H(29)	86(4)
C(13)–N(3)	134.3(4)				
Hexane-1,6-diammonium Cation					
N(1)–C(14)	149.1(4)	C(17)–C(18)	152.2(4)	N(1)–H(15)	95(5)
N(2)–C(19)	147.4(4)	C(18)–C(19)	150.2(5)	N(2)–H(16)	82(5)
C(14)–C(15)	150.6(4)	N(1)–H(14)	83(4)	N(2)–H(17)	80(5)
C(15)–C(16)	152.1(4)	N(1)–H(13)	95(3)	N(2)–H(18)	92(5)
C(16)–C(17)	150.9(4)				

The Cu^{2+} cations are linked by the $[\text{C}_6(\text{COO})_4(\text{COOH})_2]^{4-}$ anions to form infinite chain-like polyanions with a composition of $\{\text{Cu}(\text{H}_2\text{O})_2(\text{urea})[\mu_2\text{-C}_6(\text{COO})_4(\text{COOH})_2]\}_n^{2n-}$ (Fig. 3). The dihydrogen mellitate tetraanion connects two copper-ions and adopts a μ_2 coordination mode. The two carboxylate groups (C(10), C(7)) bound to Cu^{2+} are in the para position and act as monodentate ligands. Surprisingly, the deprotonated carboxylate groups with C(8) and C(12) are not connected to Cu^{2+} . The polyanionic chains extend along $[\bar{1}01]$ and they are stacked in ...ABAB... sequence in the $[010]$ direction. A π – π interaction between the aromatic C_6 -rings can be excluded, because of the large distance between each other, which corresponds to the crystallographic b-axis [58,59] (Fig. 4). The linear charge density of the polyanionic chains is $1.85 \cdot 10^{-3}$ e/pm (541 pm/unit charge). The negative charge is balanced by hexane-1,6-diammonium cations intercalated between neighbouring chains. The skeleton of the hexane-1,6-diammonium cation does not take a full all-*trans* (antiperiplanar) conformation (Fig. 5a). The ammonium group N(2) is rotated away which leads to a *synclinal* conformation as seen in the *Newman* projection along the

C(18)–C(19) bond in Fig. 5b. The C–N bond lengths are 149.1(4) and 147.4(4) pm and the C–C bonds range from 150.2(5) to 152.2 (4) pm (Tab. 2). In the crystal structure of e.g. hexane-1,6-diammonium bis(dihydrogenarsenate) [60] it was also found that the hexane-1,6-diammonium cation does not take the conformation with the lowest energy.

Coordination polymers with chain-like polyanions and intercalated organic cations are also obtained e.g. by the reaction between transition metal cations and benze-1,2,4,5-tetracarboxylic acid in the presence of amines [37,61].

< Figure 3 >

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< Figure 4 >

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Figure 5. (a) The hexane-1,6-diammonium cation (50 % probability ellipsoids, arbitrary radii for hydrogen atoms). (b) *Newman* projection along the C(18)–C(19) bond.

Table 3. Hydrogen bonds

	N...O Distance (pm)	N-H...O Angle (°)
N(1)-H(13)...O(w1)	280.6	166
N(1)-H(14)...O(7)	290.2	169
N(1)-H(15)...O(4)	286.9	164
N(2)-H(16)...O(2)	291.2	142

N(2)-H(17)...O(12)	312.4	155
N(2)-H(18)...O(7)	275.2	166
N(3)-H(27)...O(11)	305.8	150
N(3)-H(28)...O(1)*	327.9	155
N(4)-H(29)...O(w3)	293.4	162
N(4)-H(30)...O(3)*	297.7	166
	O...O Distance (pm)	O-H...O Angle (°)
O(6)-H(19)...O(12)*	253.4	172
O(10)-H(20)...O(3)*	246.5	173
O(w1)-H(21)...O(11)	281.3	155
O(w1)-H(22)...O(11)	275.4	175
O(w2)-H(23)...O(9)	293.3	173
O(w2)-H(24)...O(5)	270.1	161
O(w3)-H(25)...O(4)	292.8	164
O(w3)-H(26)...O(w1)	280.8	167

* Hydrogen bonds between neighbouring chains

The polyanion chains are linked by hydrogen bonds. The hydroxo groups O(6)–H(19) and O(10)–H(20) of the dihydrogen mellitate tetraanion form very strong hydrogen bonds to the carboxylate oxygen atoms O(12) and O(3) of neighbouring chains. The amino groups (N(3), N(4)) of the urea molecule act as proton donors in interchain hydrogen bonds to carboxylate oxygen atoms of medium and low strength. The coordinated water molecules O(w2) and O(w3) are involved in hydrogen bonds within the polyanion chain as proton donors. Additionally, O(w3) acts as proton acceptor to the amino group N(4)–H(29). The uncoordinated water molecule O(w1) and the hexane-1,6-diammonium cation stabilize the structure by strong to weak hydrogen bonds (Tab. 3). The hydrogen bonds connect the polyanion chains to a supramolecular three-dimensional network. As seen in Table 3 the deprotonated carboxylate groups C(8) and C(12), not bond to Cu²⁺, act as proton acceptors in several strong and very strong hydrogen bonds. Both the carbonyl oxygen atom O(13) and the carboxylate oxygen atom O(8) are not involved in any hydrogen bonds.

Fig. 6 shows both the XRD pattern of powdered [H₃N-(CH₂)₆-NH₃][Cu(H₂O)₂(urea)(μ₂-C₆(COO)₄(COOH)₂)]·H₂O crystals and the calculated pattern obtained from the single crystal data. As seen, the measured pattern is consistent with the calculated pattern, suggesting that the synthesis leads to a single phase product.

Figure 6. X-ray powder diffraction patterns of $[\text{H}_3\text{N}-(\text{CH}_2)_6-\text{NH}_3][\text{Cu}(\text{H}_2\text{O})_2(\text{urea})(\mu_2-\text{C}_6(\text{COO})_4(\text{COOH})_2)]\cdot\text{H}_2\text{O}$. (a) measured pattern, (b) calculated pattern.

TGA/DTA studies (Fig. 7) were carried out in air from room temperature to 1000°C at a heating rate of 10 K min^{-1} . The compound is stable up to 135°C . The following decomposition starts with an endothermic process due to the loss of water. Strong exothermic processes between approximately 240 and 660°C lead to a total weight loss of 88.1% . Between 660 and 1000°C a slight weight increase of 0.7% is observed leading to a final weight loss of 87.6% (calc. 87.4%). The residue was CuO which was identified by X-ray powder diffraction. The weight increase can be explained by a partial formation of Cu^+ during the decomposition process and the following re-oxidation in air to Cu^{2+} at high temperatures. The reduction of Cu^{2+} has also been observed during the decomposition of other copper carboxylates [62–64].

Figure 7: Thermal analysis of $[\text{H}_3\text{N}-(\text{CH}_2)_6-\text{NH}_3][\text{Cu}(\text{H}_2\text{O})_2(\text{urea})(\mu_2-\text{C}_6(\text{COO})_4(\text{COOH})_2)]\cdot\text{H}_2\text{O}$.

The IR spectrum is shown in Fig. 8. O–H and N–H stretching vibrations are in the range of 3500 to 3200 cm^{-1} . A sharp band at 2944 cm^{-1} reflects the C–H stretching mode. Bands at 1710 , 1670 , 1617 , 1580 , 1504 , 1427 , 1325 and 1144 cm^{-1} represent C–O, C–N and N–H vibrations. The compound contains three different organic molecules,

therefore an assignment in detail is not possible. Absorption bands at 1710 and 1670 cm^{-1} are due to the C–O stretching vibration of the urea carbonyl group and the COOH group of the dihydrogen mellitate tetraanion. The bands at 1580 and 1325 cm^{-1} are mainly caused by the asymmetrical and symmetrical stretching vibration of the deprotonated carboxylate groups. The N–H rocking mode appears at 1144 cm^{-1} [65–68].

Figure 8: IR spectrum of $[\text{H}_3\text{N}-(\text{CH}_2)_6-\text{NH}_3][\text{Cu}(\text{H}_2\text{O})_2(\text{urea})(\mu_2-\text{C}_6(\text{COO})_4(\text{COOH})_2)]\cdot\text{H}_2\text{O}$.

Figure 9: Susceptibility versus temperature of $[\text{H}_3\text{N}-(\text{CH}_2)_6-\text{NH}_3][\text{Cu}(\text{H}_2\text{O})_2(\text{urea})(\mu_2-\text{C}_6(\text{COO})_4(\text{COOH})_2)]\cdot\text{H}_2\text{O}$. The inset shows the magnetic moment depending on temperature.

The magnetic susceptibility of $[\text{H}_3\text{N}-(\text{CH}_2)_6-\text{NH}_3][\text{Cu}(\text{H}_2\text{O})_2(\text{urea})(\mu_2-\text{C}_6(\text{COO})_4(\text{COOH})_2)]\cdot\text{H}_2\text{O}$ was measured between 5 and 295 K (Fig. 9). The compound shows a paramagnetic behaviour. The change of the susceptibility followed the Curie-Weiss law with a Curie constant of $C = 5.86 \cdot 10^{-6}\text{ m}^3\text{ K mol}^{-1}$. The observed Weiss temperature of $\Theta = -1.47\text{ K}$ suggests a possible very weak antiferromagnetic interaction. From the Curie constant the magnetic moment is calculated as $\mu_{\text{mag}} = 1.93\text{ }\mu_{\text{B}}$ per Cu^{2+} . The slightly larger value than the theoretical spin-only one of $1.73\text{ }\mu_{\text{B}}$ for Cu^{2+} can be explained by a weak spin-orbit

interaction [69]. Magnetic moments larger than the spin-only value are usually found in Cu²⁺ complexes [70].

Conclusions

In summary, we reported on the synthesis and crystal structure of a novel one-dimensional Cu(II)-dihydrogen mellitate coordination polymer in the presence of urea as additional O-donor ligand and 1,6-diaminohexane as template agent. The connection between the Cu²⁺-ions and the dihydrogen mellitate tetraanion leads to infinite chain-like polyanions. The hexane-1,6-diammonium cations adopt a partial *synclinal* conformation and act as counter ions intercalated between neighbouring chains. The coordination polymer is thermally stable up to 135 °C and magnetic measurements reveal a paramagnetic Curie-Weiss behaviour between 5 and 295 K.

Experimental Section

Single crystals of [H₃N-(CH₂)₆-NH₃][Cu(H₂O)₂(urea)(μ₂-C₆(COO)₄(COOH)₂)]·H₂O were synthesized in the presence of 1,6-diaminohexane and urea. An aqueous solution of 5ml 0.1M Cu(NO₃)₂ was added to a solution of 5ml 0.2M 1,6-diaminohexane. A precipitate, which appeared intermediately, was dissolved by addition of a small amount of 2M HNO₃. Then a solution of 5ml 0.03M sodium benzenhexacarboxylate and 0.06 g urea were added. The resulting solution was allowed to evaporate at room temperature yielding blue, water soluble cube-like crystals. Results of elemental analysis: (molecular weight 634.01) C 35.15 (calc. 35.99); H 4.87 (4.77); N 8.81 (8.84)%. IR-ATR (cm⁻¹): 3473(m), 3375(m), 3227(m) 2944(m), 1710(w), 1670(w), 1617(s), 1580(s), 1504(w), 1427(s), 1325(m), 1188(w), 1144(w), 1085(w), 1019(w), 940(m), 865(m), 838(m), 807(w), 768(w), 722(s), 680(s), 620(m).

ATR Fourier transformed infrared (IR-ATR) measurements were carried out at room temperature using a Bio-rad FTS 25. Thermoanalytic measurements were performed in flowing air using a Netzsch STA429 device. Temperature dependent magnetizations were measured at μ₀H = 0.3 T in the temperature range of 5 to 295 K using a Quantum Design PPMS 9. The X-ray powder diffraction pattern was recorded at room temperature on a Bruker D8-Advance diffractometer, equipped with a one-dimensional silicon strip detector (LynxEyeTM) and operating with Cu-Kα radiation. X-ray single crystal structure determination was performed on a Siemens P4 four-circle diffractometer (MoKα, graphite monochromator) in a theta range up to 25.00°. Numerical absorption corrections have been applied.

An empirical extinction parameter has been introduced (0.0018(2)). The phase problem was solved by direct methods. Full matrix least squares refinement employing |F|² made use of the SHELXTL program suite [71]. Some of the hydrogen atoms have been placed into calculated positions, further hydrogen atom positions could be taken from Difference Fourier maps. They were allowed to refine

with different common isotropic displacement parameters. Crystallographic data are given in Table 4.

Further details concerning the crystal structure analysis have been deposited with Cambridge Crystallographic Data Centre, The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK, Fax +(1223)336-033, e-mail data_request@ccdc.cam.ac.uk, www.ccdc.cam.ac.uk/data_request.cif under CCDC 1060668.

Table 4. Crystallographic Data

Empirical formula	C ₁₉ H ₃₀ N ₄ CuO ₁₆
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i> (no.14)
Lattice constants	<i>a</i> = 958.48(9) pm <i>b</i> = 1465.74(11) pm <i>c</i> = 1821.14(12) pm <i>β</i> = 97.655(8)°
Cell volume	2.5357(3) nm ³
Formulas in unit cell	4
Formula weight	634.01 g/mol
Density (calc.)	1.661 g/cm ³
Wavelength	71.073 pm
Absorption coefficient	0.949 mm ⁻¹
Numerical absorption correction	min./max. transmittance
Temperature	293(2) K
Crystal size (mm)	0.28 x 0.28 x 0.58
F (000)	1316
Θ-range	2.26° – 24.99°
Limiting indices	h 0/+11; k 0/+17; l -21/+21
Reflections collected	4751
Independent reflections	4467 (R _{int} = 0.0241)
Structure solution	Direct methods
Structure refinement	Full-matrix least-squares on F ²
Refined parameters	421
Final mean shift/esd	0.002
Goodness-of-fit on F ²	1.211
Residuals (all data)	R ₁ = 0.0436 , wR ₂ = 0.0747
Max. features in last difference Fourier synthesis	342 and -363e-nm ⁻³

Acknowledgement

We are grateful to Mrs Christina Apfel for recording the thermoanalytical data.

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Figure 3. Connection between the Cu^{2+} cations and the $[\text{C}_6(\text{COO})_4(\text{COOH})_2]^{4-}$ anions viewed from [010] (urea and water molecules are omitted). Chains lying in the background are marked by darker colours.

Figure 4. Complete crystal structure of $[\text{H}_3\text{N}-(\text{CH}_2)_6-\text{NH}_3][\text{Cu}(\text{H}_2\text{O})_2(\text{urea})(\mu_2-\text{C}_6(\text{COO})_4(\text{COOH})_2)] \cdot \text{H}_2\text{O}$ viewed along [100].