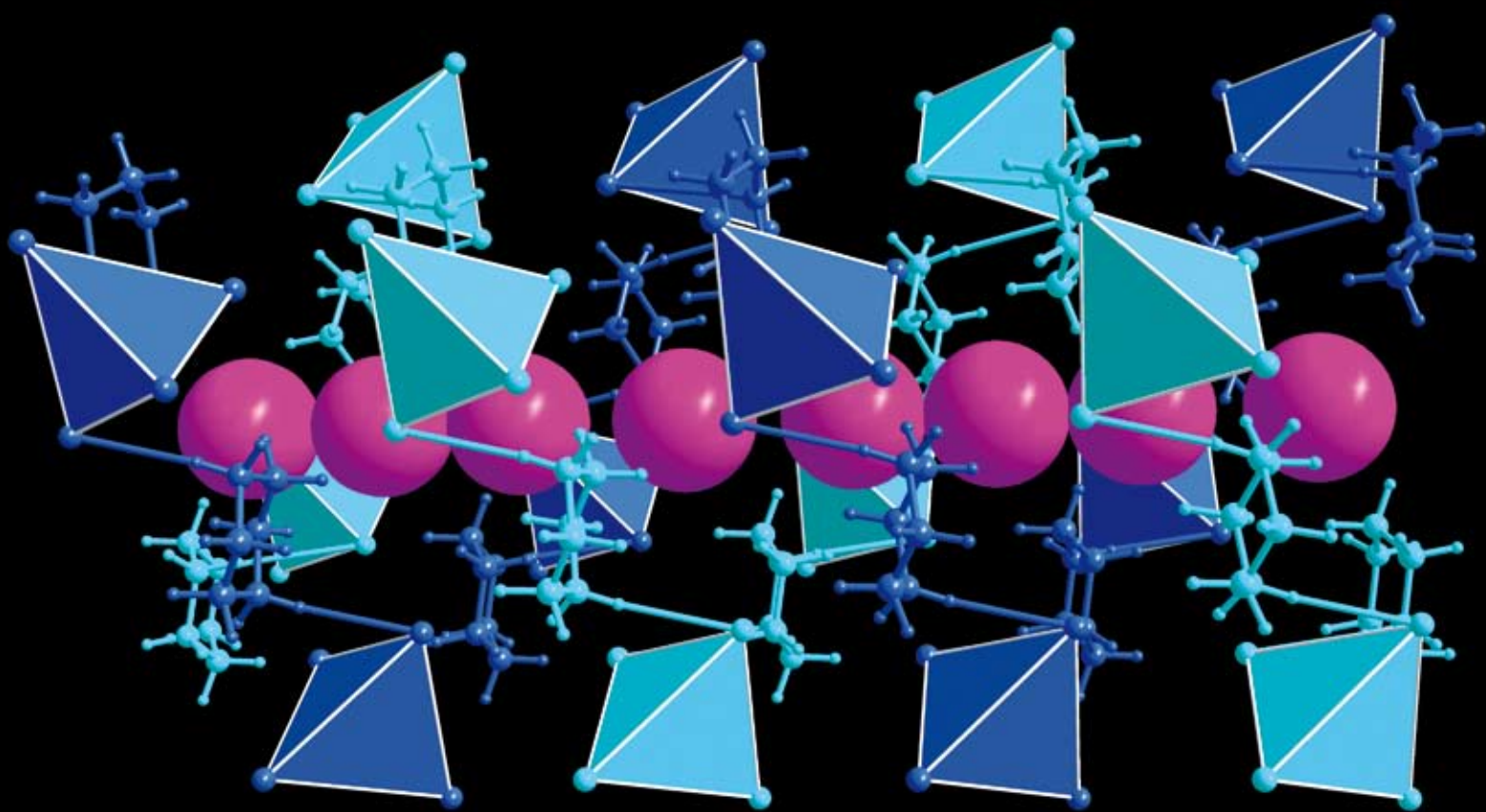


ChemComm

Chemical Communications

www.rsc.org/chemcomm

Number 16 | 28 April 2009 | Pages 2053–2224



ISSN 1359-7345

RSC Publishing

COMMUNICATION

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An inorganic starch–iodine model:
the inorganic–organic hybrid

FEATURE ARTICLE

Muhammet Uyanik
and Kazuaki Ishihara
Hypervalent iodine-mediated
oxidation of alcohols

An inorganic starch–iodine model: the inorganic–organic hybrid compound $\{(C_4H_{12}N_2)_2[Cu^I I_4](I_2)\}_n^{\dagger}$

Engelbert Redel, Caroline Röhr* and Christoph Janiak*

Received (in Cambridge, UK) 11th November 2008, Accepted 10th December 2008

First published as an Advance Article on the web 22nd January 2009

DOI: 10.1039/b820151j

The dark-blue crystal color of $\{(C_4H_{12}N_2)_2[Cu^I I_4](I_2)\}_n$, its mixture of I^- , I_3^- and linear I_4^{2-} or linear I_5^- polyiodide species in a linear channel arrangement, its channel diameter of ~ 5.5 Å and the helical arrangement of the hydrogen bonded $\{(C_4H_{12}N_2)_2[Cu^I I_4]\}^+$ supramolecular host around the channels agree with the description of the classical, yet structurally elusive, starch–iodine compound.

Polyiodides, I_n^{m-} have an extensive structural chemistry with a variety of cations.^{1–5} The well-known, yet structurally elusive, colloidal starch–iodine complex,⁶ discovered by Colin and de Claubry in 1814,⁷ is believed to consist of polyiodides in a supramolecular host–guest compound.¹ Starch which forms a very dark blue-black complex with iodine is a very sensitive test for iodine (in the likely presence of iodide).⁸ Amylose from starch is responsible for this blue polyiodide complex. In this complex amylose forms a probably left-handed helical structure of 8 Å pitch with 6 glucose units per turn. The ~ 5 Å wide central cavity of this helix may accommodate polyiodides which may consist of I_5^- , I_3^- and I_2 units modulated as $(I_2 \cdots I_3^-)_n$ or $(I_2 \cdots I^- \cdots I_2)_n$.⁶ The average I···I distances of 3.1 Å between these units are shorter than van der Waals contacts and, therefore, charge delocalization can occur along the chain which explains the intense chromophore absorbing around 600 nm (Fig. S11, ESI†).^{1,6,14}

Here we present the dark-blue inorganic–organic hybrid compound $\{(C_4H_{12}N_2)_2[Cu^I I_4](I_2)\}_n$ (**1**) (Fig. 1) as a model for the structurally unknown starch–iodine complex. Compound **1** formed under hydrothermal conditions from comproportionation of $Cu^{II}O$ and Cu^0 in a mixture of HI (57 wt%), I_2 and piperazine, $C_4H_{10}N_2$.† The crystal structure of **1** contains isolated tetraiodocuprate(I) anions, $[Cu^I I_4]^{3-}$, piperazinium dications, $(C_4H_{12}N_2)^{2+}$ and what appears to be chains of equidistant iodine atoms along $(1/4, 1/4, z$ and $3/4, 3/4, z)$ (Fig. 2).‡

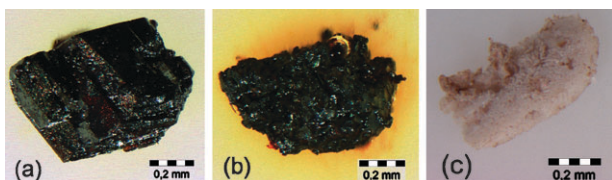


Fig. 1 (a) Dark-blue crystal of compound **1**. (b) Crystal degradation in water or alcohols through leaching of iodine, I_2 into solution. (c) Amorphous (from XRPD) residue before complete dissolution.

Institut für Anorganische und Analytische Chemie, Universität Freiburg, Albertstr. 21, D-79104 Freiburg, Germany.

E-mail: janiak@uni-freiburg.de; E-mail: caroline@ruby.uni-freiburg.de; Fax: +49 (0)761 2036147; Tel: +49 (0)761 2036127

† Electronic supplementary information (ESI) available: Synthesis, elemental analyses, IR, full Raman, XRPD, ESR, TG–DTA, EDS–SEM, iodine–starch reaction. CCDC 708974. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b820151j

The shape of the electron density around the ideal position $1/4, 1/4, 1/4$ (intersection of two 2_1 axes) of the I_2 atoms in the channels of **1** (Fig. 2) suggests a statistical disorder within the iodine chain, thus yielding only an average distance of 3.39 Å. From the subsequent split position refinement of the I_2 site probable I···I distances of 2.76, 3.39 and 4.02 Å can be deduced and also intermediate values of 3.07 and 3.70 Å if the center of the split position is considered as well (Fig. 3).

However, the diffraction images of the studied crystal with the partially ordered iodine structure showed eight additional maxima in the vicinity of each Bragg peak that could be indexed by the introduction of a q -vector of 0.2, 0.2, 0.38. Based on the fact that a modulation vector with three components is required, not only an incommensurate ordering of the polyiodide species in one channel but in addition a correlation between the occupation of neighboring channels can be assumed.

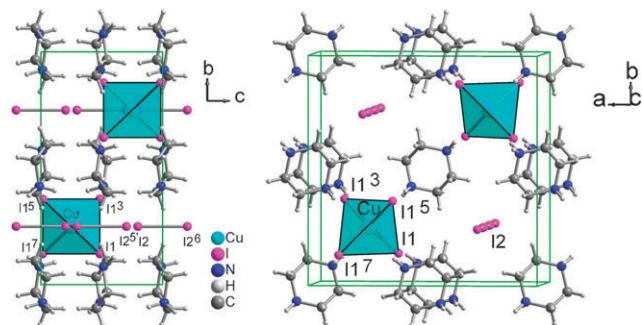


Fig. 2 Unit cell packing of **1**. Selected distances (Å) and angles (°): Cu–I1 2.677(2), I2–I2⁶ 2.755(5), I2–I2^{5'} 0.631(5), I1–Cu–I1³ 107.22(6), I1–Cu–I1⁵ 110.61(3), I2^{5'}–I2–I2⁶ 180; symmetry transformation: 3 = 1.5 – x, 0.5 – y, z; 5 = x, 0.5 – y, 0.5 – z; 5' = x, 0.5 – y, 1.5 – z; 6 = y, x, 2 – z; 7 = 1.5 – x, y, 0.5 – z.

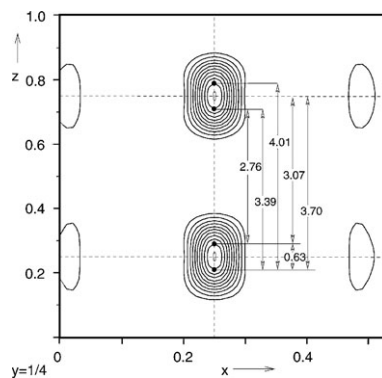
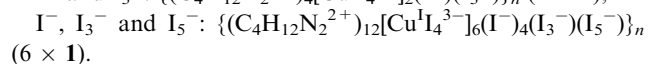
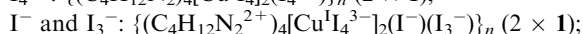
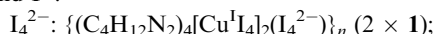


Fig. 3 Difference Fourier synthesis of the average structure calculated without the I_2 atom (isolines with $5 e \text{ \AA}^{-3}$; dark points: position of the I_2 atoms in the final split atom refinement).

From the charge balance in the sum formula of **1**, $\{(C_4H_{12}N_2^{2+})_2[Cu^I I_4^{3-}](I_2^-)\}_n$ two iodine atoms share a single negative charge, (I_2^-) . The inter-iodine distance of 3.39 Å in the channels of **1** is indicated in the X-ray patterns by diffuse lines suggesting statistical disorder within the iodide chain, thus, yielding only an average distance (Fig. 2 and 3).[†] With respect to the tetrahedral tetraiodocuprate(i) moiety in **1** we note that we are not aware of any other structurally authenticated halocuprate with isolated metal tetrahedra.⁹ Edge- and corner-sharing polyhedra prevail in halometallates.¹⁰ In particular no isolated $[CuI_4]^{3-}$ is known.¹¹

Compound **1** is shown by X-ray powder diffraction to be a pure phase and by ESR to contain only Cu(I) (Fig. S5 and S6 in ESI[†]). One of the best analytical methods to study polyiodide species is Raman-Fourier transform (FT) spectroscopy. The Raman-FT spectrum of **1** displays strong maxima at 109 and 168 cm^{-1} (Table 1, Fig. 4) due to the symmetric stretching vibrations of the linear and symmetric I_3^- and I_4^{2-} or I_5^- . The maxima at 86 and 140 are due to $[CuI_4]^{3-}$,¹² with some possible contribution to the peak at 140 from slightly asymmetric I_3^- . From the Raman study free iodine, I_2 or I_2 only loosely coordinated to iodide does not seem to be present (Table 1). Hepta-iodide, I_7^- and higher polyiodides are excluded because they are not known in a linear arrangement. Thus, the iodide chains $(I_2^-)_n$ in **1** are described as incommensurate polyiodide chains of linear I_4^{2-} or I_5^- , I_3^- and I^- units. While penta-iodide is better known in its more common bent forms,¹ examples of linear I_5^- have been reported (Table 1).

Charged-balanced sum formulae of **1**, $\{(C_4H_{12}N_2)_2[Cu^I I_4](I_2)\}_n$ can be described with I_4^{2-} or with mixtures of linear I_5^- , I_3^- and I^- :



Resonance Raman spectra of the starch-iodine complex display four characteristic maxima¹³ at 24, 52, 112 and 164 cm^{-1} which have been assigned to stretching and bending vibrations of the polyiodide chain. The polyiodide species in the amylose-iodine complex is certainly not simply I_3^- . It is more likely that the species in the starch-iodine complex are $(I_2 \cdots I_3^-)_n$ or $(I_5^-)_n$.¹⁴

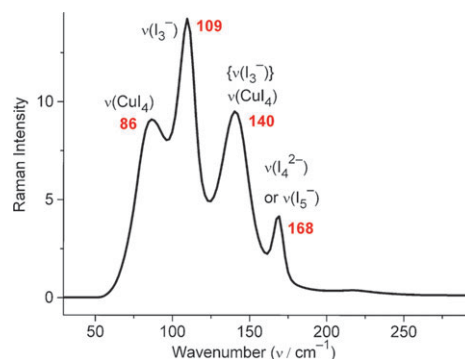


Fig. 4 Raman-FT spectrum of **1** with assignment.

In $(Me_4Sb)_3I_8$ a superficially similar, linear ordered iodine atom chain structure has been proposed with slightly alternating $I \cdots I$ distances of 3.283(2) and 3.299(2) Å (*cf.* 3.39 Å in **1**).¹⁵ From the charge balance and from the thermal ellipsoids presented in $(Me_4Sb)_3I_8$, the $(I_8^{3-})_n$ chains are likely to be incommensurate chains of polyiodide species as in **1**.

Even today, the exact structure of the starch- or amylose-iodine complex is not really known.⁶ An X-ray powder pattern of the amylose-iodine complex can be indexed using a hexagonal cell ($\gamma = 120^\circ$) with $a = b = 12.97$, $c = 7.91$ Å (*cf.* **1**, tetragonal $a = b = 12.98$, $c = 6.78$ Å).¹⁶ As a model to the elusive starch-iodine complex crystalline Na^+ , Ba^{2+} and Cd^{2+} salts of α -cyclodextrin-iodide structures have been studied.¹⁷ The cyclodextrin for the structural model studies consists of α (1-4)-linked six-membered cyclic glucose rings. Yet, they lack the helical arrangement of amylose.

In **1** the N-H \cdots I hydrogen bonding from the piperazinium dications to the tetraiodocuprate anion leads to helical arrangements of two interdigitated fourfold helices around each polyiodide chain. Adjacent polyiodide chains are surrounded by alternating right-handed (*P*) 4_1 or left-handed (*M*) 4_3 helices, which wrap around the channels in the *c* direction (Fig. 5). These helices enclose a channel diameter of ~ 5.5 Å (inter-atomic distance) in **1**, to be compared with the channel diameter of ~ 5.2 Å in $[Cd^{2+}-\alpha$ -cyclodextrin-polyiodide],¹⁴ which is regarded as a good model of the starch-/amylose-iodine complex.

Table 1 Raman bands and $d(I-I)$ of linear polyiodides I_3^- , I_4^{2-} and I_5^-

Compound (reference)	$d(I-I)/\text{Å}$	ν/cm^{-1}	Compound (reference)	$d(I-I)/\text{Å}$	ν/cm^{-1}
Free I_2 ¹⁸	2.670	180s	$[I \cdots I \cdots I]^{2-} = I_4^{2-}$ (symm.) in $[(C_5H_7N_2Se)_2](I_3)(1/2 I_4)$ ²⁰	2.819, 3.405	155s
Weakly bound I_2 in $[mo_2ttl]_2I_{16}$, ^{b,19} $[Ag_2([15]aneS_5)_2]I_{12}$, ^{c,3} $[K([15]aneO_5)_2]I_9$, ^{c,27}	2.741, 2.755, 2.716	174s, 172brs, 180brs			
$[I-I-I]^- = I_3^-$ (slightly asymm.) in $[n-Bu_4N](I_3)$ ²¹	2.890, 2.950	108s	$[I \cdots I \cdots I]^{2-} = I_4^{2-}$ (symm.) in $[Cd(NH_3)_4I_2 \cdot I_2]$ ²²	2.793, 3.386	Not det.
$[I-I-I]^- = I_3^-$ (symm.) in $[bis(DMT-TTF)](I_3)(I_5)$, ^{d,23}	2.929	110s, (324w)	$[I-I \cdots I \cdots I]^- = I_5^-$ (symm.) in $[bis(DMT-TTF)](I_3)(I_5)$, ^{d,23}	2.785, 3.191	163m, (304 w)
I_3^- in (1,1'-(propane-1,3-diyl) ferrocenium) ₃ (I_3) ₂ (I_5) ²⁴	2.889, 2.967	Not det.	I_5^- in (1,1'-(propane-1,3-diyl) ferrocenium) ₃ (I_3) ₂ (I_5) ²²	2.800, 3.220	Not det.
$[I-I-I]^- = I_3^-$ (slightly asymm.) in $Pd_2Cl_2([15]aneN_4)(I_3)_2$, ^{e,25}	2.871, 2.953	107s, 135w	$[I-I \cdots I \cdots I]^- = I_5^-$ (symm.) in $(TMA \cdot H_2O)_{10} H^+ I_5^-$, ^{f,26}	2.740, 3.260	(75vw) ²¹ , 163s
$[I-I-I]^- = I_3^-$ (slightly asymm.) in $[Pd_2Cl_2([18]aneN_2S_4)]_{1.5} I_5(I_3)_2$, ^{g,27}	2.904–2.929, 2.948–2.959	108s, 138w			

^a br = broad, s = strong, m = medium, w = weak. ^b mo_2ttl = 3,5-bis(*N*-morpholinio)-1,2,3-trithiolate. ^c $[15]aneO_5$ or $[15]aneS_5$ = 1,4,7,10,13-pentaoxa or pentathiocyclopentadecane. ^d Bis(dimethylthio)tetrathia-fulvalene (DMT-TTF) bisannulated tetraoxatetrathiatetracosane. ^e $[15]aneN_4$ = 1,4,8,12-tetraazacyclopentadecane. ^f TMA = trimesic acid. ^g $[18]aneN_2S_4$ = 1,4,10,13-tetrathia-7,16-diazacyclooctadecane.

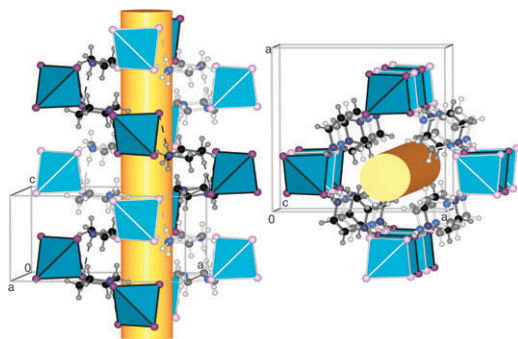


Fig. 5 Helical arrangement in **1** shown in [100] and [001]. Hydrogen bonds as dashed lines (N)H1...I1 2.61, N...I1 3.51(2) Å, N–H1...I1 173.7°. The polyiodide chains are depicted as yellow columns.

When crystals of **1** are immersed in water or other polar solvents (methanol, ethanol) in the presence of air, yellow-brown iodine, I₂, leaches from them to give a near-colorless amorphous solid which eventually also dissolves (Fig. 1). The deep blue color of starch–iodine also disappears when air is bubbled through its colloidal solution under light due to the oxidation of I[−] to I₂.⁸

The dark-blue crystal color of **1**, its polyiodide species in a linear channel arrangement, the channel diameter, and the helical arrangement of the supramolecular host around the channels suggest that the description of the inorganic–organic hybrid compound $\{(C_4H_{12}N_2)_2[CuI_4](I_2)_n\}$ (**1**) as the first inorganic–organic hybrid model for the classical starch–iodine compound is justified.

We thank M. Welschehold, S. Steimle, D. Gnant, T. Engesser, M. Wendorff and Dr H. Müller-Sigmund for their help and DFG grant Ja466/41-1.

Notes and references

† X-Ray structure determination: C₈H₂₄N₄CuI₆, 1001.25 g mol^{−1}, tetragonal, *P*₄₂/*nmn* (134), *Z* = 2, 203(2) K on a Bruker ApexII CCD, 4.44° ≤ 2θ ≤ 51.68°, ω-scans, *a* = *b* = 12.9597(4), *c* = 6.7723(3) Å, *V* = 1137.43(7) Å³, *D*_{calc.} = 2.923 g cm^{−3}, crystal size 0.20 × 0.17 × 0.12 mm, *F*(000) 894, 3770 reflections measured, 590 independent (*R*_{int} = 0.0313), μ(Mo–Kα) (λ = 0.71073 Å), 29 refined parameters, *R*₁ = 0.0631, *wR*₂ = 0.1677 for 489 reflections with *I* > 2σ(*I*), *R*₁ = 0.0720, *wR*₂ = 0.1734 for all data, goodness-of-fit 1.111. All non-hydrogen atoms refined anisotropically.

Due to the variable disorder in the channels (see structure description above), several crystals of **1** were tested and measured on different diffractometers (STOE-IPDS-II, Bruker APEXII CCD) and at different temperatures. The diffraction patterns of several other crystals of lower quality exhibit additional diffuse streaks along the *c** direction and the analysis of their Bragg reflections reveals only a continuous tube of electron density along the 1/4, 1/4, *z* direction. Nevertheless, this also integrates to exactly two iodine atoms per channel. Only after several trials one crystal could be isolated that does not show diffuse scattering. However, the diffraction images of this crystal showed eight additional intensity maxima in the vicinity of each Bragg peak. These extra peaks could be indexed with the *q*-vector 0.2, 0.2, 0.38. The solution of the modulated structure in four-dimensional space will be the subject of subsequent studies.

Currently, the structure was solved by direct methods (program SHELXS-97) using the Bragg reflections of the small tetragonal unit cell only. All non-hydrogen atom positions, including a single I atom at the Wyckoff site 4c representing the iodine species in the channels, were first refined anisotropically by full-matrix least squares methods on *F*² (SHELXL-97). Due to the strong anisotropy of the thermal parameters of this position, a detailed inspection of the electron density inside the channel was carried out using the program JANA2000 (see Fig. 3).²⁸ The shape of the electron density suggested the use of a split position for the I2 atom in the final refinement of the average structure. A free refinement of the occupation of the I2 position reveals exactly 2 iodine atoms per channel and thus a mean distance of the I atoms of 3.39 Å, which is in good

agreement with the chemical analysis (Cu–I = 1 : 6, see ESI†) and the iodine species detected using Raman spectroscopy (see above).

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