Iodoargentates and Cuprates Stabilized by Sulfonium Cations With Long Alkyl Chains

Heléne Paulsson,*[a] Malin Berggrund,[a] Andreas Fischer,[a] and Lars Kloo[a]

Keywords: Cations / Iodide / Copper / Silver / Crystal structure

$[DodMe_2S]_2AgI_3$ and $[DodMe_2S]Ag_2I_3$ were obtained from mixtures of dodecyldimethylsulfonium iodide and silver iodide in acetonitrile solution. $[DodMe_2S]_2AgI_3$ crystallizes in the orthorhombic crystal system, space group *Pbca* and contains trigonal planar anions AgI_3^{2-}, while $[DodMe_2S]Ag_2I_3$ crystallizes in the triclinic crystal system, space group $P\bar{1}$, and consists of polymeric anions $^1_\infty(Ag_2I_3)^-$. In both structures, the sulfonium cations form a layer of parallel and interpenetrating dodecyl chains with the sulfoniumdimethyl groups on both sides of the layer. $[DodMe_2S]_2CuI_3$ was obtained from dodecyldimethylsulfonium iodide and copper iodide mixtures and is isostructural with the corresponding silver compound.

Introduction

Metal iodides and polyiodides are interesting and important materials that are useful in various electrochemical applications.[1−4] In our laboratory, many alkyl iodide and polyiodide compounds have been synthesized in sulfonium-based reaction media, which have emerged as efficient electrolytes in dye-sensitised nanostructured solar cells of the Grätzel type.[5−7] While iodometallates with symmetric cations, such as trimethylsulfonium and triethylsulfonium ions, have been prepared previously, sulfonium cations with long-chain substituents, such as dodecyl and hexadecyl groups, have not been investigated so far. $[DodMe_2S]I$ is the only compound known in this field that has been structurally characterized.[5] This is rather surprising since these long chains would introduce new properties into the materials, yielding compounds that may combine the polarity of a halometallate and the nonpolar properties of the alkyl groups.

Low-dimensional compounds, such as hybrid organic-inorganic layered solids, have been shown to combine conductivity and magnetism or optics and magnetism.[8−11] Several inorganic host networks with structural flexibility of the interlayer separation have been investigated and large organic anions (amphiphiles) been successfully inserted. These amphiphiles may be formed from long-chain alkyl compounds with charged, polar endings consisting of ammonium-, phosphonium- or sulfate-based complexes. The long-chain alkyl groups form mono- or bilayers, which are favourably close-packed.[12−15] In amphiphiles with polar sulfonium groups, the structure of the packed alkyl layers is preferably tilted. This has been observed in both hydroxide double salts and highly conducting, so called Longmuir−Blodgett films.[13−14]

The main purpose of this work is to investigate metal-iodide-doped long-chain alkyl sulfonium iodides, with and without additional iodine. One experimental difficulty that is inherent in these systems is imposed by the physical properties, such as very high viscosities, which makes it difficult to obtain crystals with a sufficiently high quality for structure determinations. This problem may be diminished, though, by use of organic solvents such as acetone or acetonitrile. From using systems of metal-iodide-doped asymmetric trialkylsulfonium iodides, we have obtained the new compounds $[DodMe_2S]_2AgI_3$, $[DodMe_2]Ag_2I_3$ and $[DodMe_2S]_2CuI_3$, whose structures are presented here.

Results and Discussion

Crystal Structure of $[DodMe_2S]_2CuI_3$ and $[DodMe_2S]_2AgI_3$

Both compounds are isostructural and crystallise in the orthorhombic crystal system, space group *Pbca*. The structures consist of dimethyldodecylsulfonium cations and approximately trigonal planar MI_3^{2-} anions (M = Ag, Cu). Figure 1 shows the arrangement of both structures in the unit cell. The cations are arranged in such a way that all dodecyl chains are zigzag shaped and run parallel to each other, thus forming laminar layers with the SMe_2 groups sticking out on both sides of the surfaces;[5] the MI_3^{2-} anions are found between the layers. The geometry of the MI_3 groups is almost trigonal planar with bond lengths between 2.523(2) and 2.561(2) Å in CuI_3^{2-}. In AgI_3^{2-} the

---

[a] Dept. of Chemistry, Inorganic Chemistry, The Royal Institute of Technology (KTH),
Teknikringen 36, 10044 Stockholm, Sweden
Fax: (internat.) + 46-8/7909349
E-mail: Larsa@inorg.kth.se

range of interatomic distances is between 2.703(2) and 2.757(2) Å. The angles between the metal-iodine bonds are between 115.7(1) and 123.9(1)° (Cu) and 114.20(6) and 125.55(2)° (Ag). Thus, the arrangement around the central metal atoms deviates significantly from the ideal trigonal geometry.

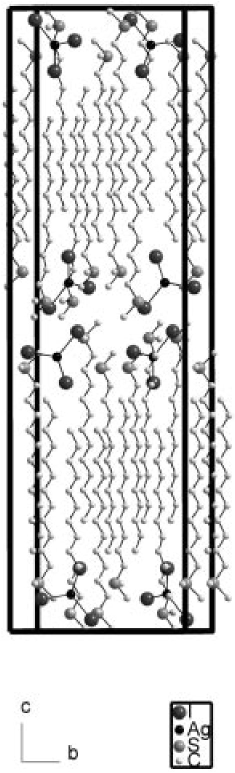

Figure 1. Structure of $[DodMe_2S]_2CuI_3$ and $[DodMe_2S]_2AgI_3$

While three-coordinate copper(I) appears frequently, this particular structural motif is not very common in the structural chemistry of discrete iodocuprates(I) and -argentates(I). So far, only one example of a compound containing AgI_3^{2-} anions has been published, namely in the structure of methyltriphenyl phosphonium triiodoargentate.[16] The geometry of the anion in this compound is in very good agreement with that in our study. In the case of iodocuprates, several examples of structures containing CuI_3 groups are known in compounds such as methyltriphenylphosphonium triiodocuprate[17] or cobaltocenium triiodocuprate.[18] Additionally, similar compounds for Cu^{II}, containing the CuX_3^- anion (X = Cl, Br), have been published recently.[19] The CuX_3^- conformation deviates from a perfect trigonal structure, as expected, due to potential Jahn-Teller instability. Also, due to the inherent instability of Cu^{II} in the presence of iodide, similar CuI_3^- ions are not known.

Crystal Structure of $[DodMe_2S]\ {}^1_\infty[Ag_2I_3]$

This compound crystallizes in the triclinic crystal system, space group $P\bar{1}$. It contains a polymeric structure consisting of one-dimensional, infinite Ag_2I_3 chains. These chains are made from two rows of edge-sharing AgI_4 tetrahedra, which are connected by common tetrahedron edges (Figure 2). The $Ag_2I_3^-$ anion is also present in the structures of $[NMe_4]Ag_2I_3$[20] and $CsAg_2I_3$.[21] Several iodocuprate(I) analogues are known, such as $CsCu_2I_3$ and RCu_2I_3 (R = *N*-methylpyridinium).[22–23]

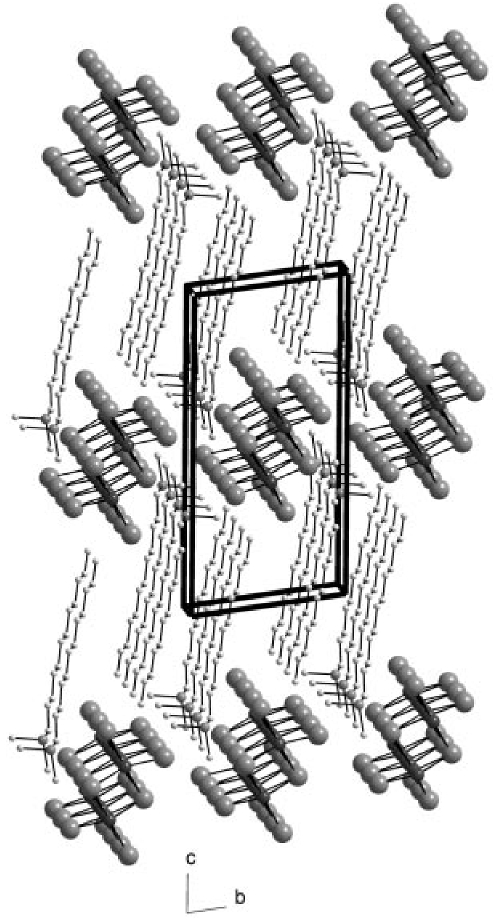

Figure 2. Structure of $[DodMe_2S]\ {}^1_\infty[Ag_2I_3]$

As in other polymeric anions of this type, the arrangement of the iodide ions around the silver ions is rather distorted. The I−Ag−I angles lie in a range of 100.0° to 119.7°, thus deviating significantly from the ideal tetrahedral coordination. The bond lengths illustrate the different nature of the two types of iodide ions that are present. Each I(1) connects four silver atoms and thus forms the corner of four common tetrahedra. The interatomic I(1)−Ag distances are therefore rather long (288.4−299.6 pm). I(2) and I(3) connect two silver ions and the distances between these iodide ions and the silver ions are in the range 279.7−283.0 pm.

Conclusions

Silver- and copper-iodide-containing dodecyldimethylsulfonium iodides are structurally stabilized by lamellar networks formed by the long-chain dodecyl groups in $(DodMe_2S)^+$ cations, whereas the anionic building blocks may consist of either monomeric entities, such as AgI_3^{2-} and CuI_3^{2-}, or polymeric structures such as $Ag_2I_3^-$. The AgI_3^{2-} anions are preferably formed in the presence of elemental iodine. The structure of $[Ag^+(I^-)_3]^{2-}$ reveals that iodide ions obviously prefer silver ions to iodine molecules, since triiodide ions $(I_3)^-$ should otherwise be expected to form. Comparatively, thallium triiodide (TlI_3) has shown other properties since its crystal structure actually consists of Tl^+ and $(I_3)^-$ units.[5,24−25]

Experimental Section

General Remarks: The crystals for crystallographic analysis were grown as "hermits" in order to give maximum quality, and consequently the yield was not optimised. Bulk synthesis of the compounds typically produces a yield of about 70−80%. The purity of the products was checked by NMR and Raman spectroscopy as well as by a melting point determination.

Synthesis of $[DodMe_2S]_2CuI_3$ and $[DodMe_2S]_2AgI_3$: Crystals of $[DodMe_2S]_2CuI_3$ and $[DodMe_2S]_2AgI_3$ could be obtained by reacting dodecyldimethyl sulfonium iodide with the respective metal iodide in the sulfonium-to-metal-iodide proportion 1:0.3 and then dissolving the mixtures in an acetonitrile solution. The $[DodMe_2S]I$ used was synthesized by reacting equimolar amounts of dodecylmethyl sulfide and methyl iodide (see ref.[7]) Concerning the AgI_3-containing crystals, elemental iodine was also added in the sulfonium-to-iodine proportion 1:0.01. Upon slow evaporation of the solvent at room temperature, both compounds crystallized within a couple of days. In a typical synthesis, 10 mg of the respective mixture was dissolved in 0.1 mL acetonitrile and then left in an NMR tube for slow evaporation at room temperature yielding 6 mg (60%) of white or light yellow crystals.

Synthesis of $[DodMe_2S]Ag_2I_3$: White crystals of $[DodMe_2S]Ag_2I_3$ could be obtained from mixtures of $[DodMe_2S]I$ and silver iodide (AgI) in a similar way as mentioned above, though without any addition of iodine [yield: about 6 mg (60%)].

Crystal Structure Determination of $[DodMe_2S]_2CuI_3$ and $[DodMe_2S]_2AgI_3$: X-ray diffraction data for the crystals were collected using a Bruker Nonius KappaCCD diffractometer. Both compounds crystallise in the orthorhombic system. The space group *Pbca* could be unambiguously determined from the systematic absences. Numerical absorption corrections were applied[26] The positions of the Cu (Ag) and I atoms were determined by direct methods, and C and S atoms were localized in subsequent difference Fourier syntheses. Hydrogen atoms were placed at calculated positions and refined using a riding model. All parameters were refined against F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystallographic details of the structure determinations are presented in Table 1.

Crystal Structure Determination of $[DodMe_2S]^1{}_\infty[Ag_2I_3]$: X-ray diffraction data were collected by using a Bruker Nonius KappaCCD diffractometer. The compound crystallises in the triclinic system; the space group $P\bar{1}$ could be confirmed during the structure determination. A numerical absorption correction was applied[26] The positions of Ag and I atoms were determined by direct methods,

Table 1. Crystallographic data, details of data collection and structure refinement calculations for $[DodMe_2S]_2CuI_3$ (**1**), $[DodMe_2S]_2AgI_3$ (**2**) and $[DodMe_2S]\ {}^1{}_\infty[Ag_2I_3]$ (**3**)

Compound number	**1**	**2**	**3**
Empirical formula	$C_{28}H_{62}CuI_3S_2$	$C_{28}H_{62}AgI_3S_2$	$C_{14}H_{31}Ag_2I_3S$
Unit cell dimensions/pm	$a = 971.66(3)$ $b = 1504.91(3)$ $c = 5232.0(2)$ p	$a = 974.93(3)$ $b = 1515.14(3)$ $c = 5252.0(2)$	$a = 683.53(6)$ $b = 914.69(6)$ $c = 1937.6(2)$ $\alpha = 81.798(3)°$ $\beta = 81.748(3)°$ $\gamma = 88.568(4)°$
Cell volume/10^6 pm^3	$V = 7650.6(4)$	$V = 7758.0(4)$	$V = 1186.6(2)$
Z	8		2
ρ(calcd.)/g·cm^{-3}	1.575	1.629	2.317
Crystal system, space group	orthorhombic, *Pbca* (No. 61)		triclinic, $P\bar{1}$ (No. 2)
Diffractometer	Bruker Nonius KappaCCD		
Temperature/K	297	297	297
Radiation	Mo-$K\alpha$, $\lambda = 71.073$ pm		
Absorption coefficient/ cm^{-1}	$\mu = 31.2$	$\mu = 30.3$	$\mu = 56.3$
Absorption correction	numerical		
Theta range	$8.16° < 2\theta < 52.72°$	$10.22° < 2\theta < 50.08°$	$10.24° < 2\theta < 56.56°$
Number of measured reflections	56315	58846	12942
Number of unique reflections	7757	6646	5662
R_{int}	0.0897	0.0577	0.0361
Number of refined parameters	307	307	182
Ratio reflections/parameters	25	21	31
Residuals R_1 (all reflections)[a]	0.112	0.0735	0.0870
R_1	0.0536 (4688 obsd. reflns.)	0.0459 (4887 obsd. reflns.)	0.0409 (3516 obsd. reflns.)
wR_2 (all reflections)[b]	0.0808	0.0852	0.101
Difference electron density	+0.75/−0.71	1.15/−0.73	+1.08/−1.32
CCDC number	198736	198737	198735

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma w(F_o^2)^2]^{0.5}$.

and C and S atoms were localized in subsequent difference Fourier syntheses. Hydrogen atoms were placed at calculated positions and refined using a riding model. All parameters were refined against F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystallographic details of the structure determinations are presented in Table 1.

CCDC-198735, -198736, and -198737 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

The Swedish National Research Council is acknowledged for financial support and for the funding of the Bruker Nonius KappaCCD diffractometer.

---

[1] H. Stegemann, K.-F. Tebbe, L. A. Bengtsson, *Z. Anorg. Allg. Chem.* **1995**, *621*, 165−170.
[2] K.-F. Tebbe, R. Buchem, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1345−1346.
[3] P. H. Svensson, L. Kloo, J. Rosdahl, *Chem. A. Eur. J.* **1999**, *5*, 305−311.
[4] P. H. Svensson, L. Kloo, *Inorg. Chem.* **1999**, *38*, 3390−3393.
[5] P. H. Svensson, *PhD Thesis*, University of Lund **1998**.
[6] H. Paulsson, A. Hagfeldt, L. Kloo, paper to be published.
[7] H. Paulsson, M. Berggrund, A. Fischer, A. Hagfeldt, L. Kloo, paper to be published.
[8] J. F. Nicoud, *Science* **1994**, *263*, 636.
[9] P. Day, *Mol. Cryst. Liq. Cryst.* **1997**, *305*, 533−542.
[10] P. Gütlich, *Mol. Cryst. Liq. Cryst.* **1997**, *305*, 17−40.
[11] L. Ouahad, *Chem. Mater.* **1997**, *9*, 1909−1926.
[12] J. S. Miller, M. Drillon, *Magnetism: Molecules to Materials II*, Wiley-VCH, **2001**.
[13] T. Bjørnholm, T. Hassenkam, N. Reitzel, *J. Mater. Chem.* **1999**, *9*, 1975−1990.
[14] M. Meyn, K. Beneke, G. Lagaly, *Inorg. Chem.* **1993**, *32*, 1209−1215.
[15] V. Laget, C. Hornick, P. Rabu, M. Drillon, P. Turek, R. Ziessel, *Adv. Mater.* **1998**, *10*, 1024−1028.
[16] G. A. Bowmaker, A. Camus, B. W. Skelton, A. H. White, *J. Chem. Soc., Dalton Trans.* **1990**, *3*, 727−731.
[17] G. A. Bowmaker, G. R. Clark, D. A. Rogers, A. Camus, N. Marsich, *J. Chem. Soc., Dalton Trans.* **1984**, *1*, 37−45.
[18] H. Hartl, I. Bruedgam, *Z. Naturforsch., Teil B* **1989**, *44(8)*, 936−941.
[19] C. Hasselgren, S. Jagner, I. Dance, *Chem. A Eur. J.* **2002**, *8*, 1269−1278.
[20] J. K. Kildea, B. W. Skelton, A. H. White, *Austr. J. Chem.* **1986**, *39*, 171−175.
[21] C. Brink, N. F. Binnendijk, J. van de Linde, *Acta Crystallogr.* **1954**, *7*, 176−180.
[22] H. Hartl, F. Mahdjour-Hassan-Abadi, *Z. Naturforsch., Teil B* **1984**, *39*, 149−156.
[23] N. Jouini, L. Guen, M. Tournoux, *Rev. Chim. Miner.* **1980**, *17*, 486−491.
[24] P. H. Svensson, G. Raud, L. Kloo, *Eur. J. Inorg. Chem.* **2000**, *6*, 1275−1282.
[25] K. F. Tebbe, U. Georgy, *Acta Crystallogr., Sect. C* **1986**, *42*, 1675−1678.
[26] W. Herrendorf, H. Bärnighausen, HABITUS, a program for numerical absorption correction, Universities of Karlsruhe and Giessen, **1997**.

Received December 6, 2002