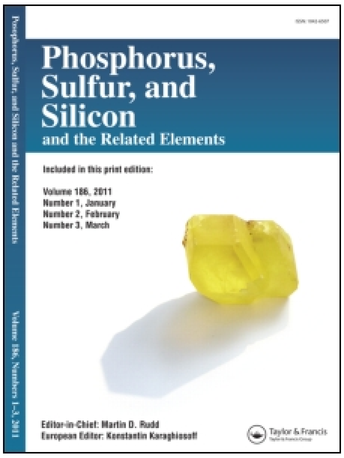
This article was downloaded by:
On: *28 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

New Oxonium Halochalcogenates(IV) and -(II)

Bernt Krebs; Illenora Beckmann; Stefan Bonmann; Sven Hasche; Oliver Reich

To cite this Article Krebs, Bernt , Beckmann, Illenora , Bonmann, Stefan , Hasche, Sven and Reich, Oliver(1998) 'New Oxonium Halochalcogenates(IV) and -(II)', Phosphorus, Sulfur, and Silicon and the Related Elements, 136: 1, 513 — 516

To link to this Article: DOI: 10.1080/10426509808545985

URL: http://dx.doi.org/10.1080/10426509808545985

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phosphorus Sulphur and Silicon
Vols. 136, 137 & 138 pp. 513–516
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint
Printed in Malaysia

NEW OXONIUM HALOCHALCOGENATES(IV) AND -(II)

BERNT KREBS, ILLENORA BECKMANN, STEFAN BONMANN,
SVEN HASCHE, OLIVER REICH,
Anorganisch-Chemisches Institut der Universität Münster,
Wilhelm-Klemm-Str. 8, D-48149 Münster

The reported novel compounds $[H_3O\cdot(\text{dibenzo-18-crown-6})][Te_2Br_9]$, $[H_5O_2][Te_2Cl_9]\cdot 2C_4H_8O_2$ and $[H_5O_2\cdot(\text{bis-dibromo-dibenzo-24-crown-8})]_2[Se_3Br_8]$ highlight the large structural and chemical variety of halogen chalcogen chemistry. Both $[Te_2X_9]^-$ anions (X = Cl, Br) consist of one square pyramidal TeX_5 fragment connected to a TeX_6 octahedron by a common edge. The linear $[Se_3Br_8]^{2-}$ anion is built by three square planar $SeBr_4$-fragments. The three counterions offer a convenient possibility for controlled synthesis of supramolecular oxonium systems.

Keywords: crystal structure; chalcogenates; oxonium ions; crown ether

INTRODUCTION

Reactions of chalcogen tetrahalides with aqueous HX usually yield the anions $[AX_6]^{2-}$, $[A_2X_{10}]^{2-}$, or $[A_3X_{13}]^-$, which can be described as fragments of the cubane-like structures of $(AX_4)_4$ (A = Se, Te; X = Cl, Br) [1-3]. During our research on anions that do not fit into this scheme we were able to synthesize three novel examples of halochalcogenates with interesting supramolecular oxonium systems as counter ions.

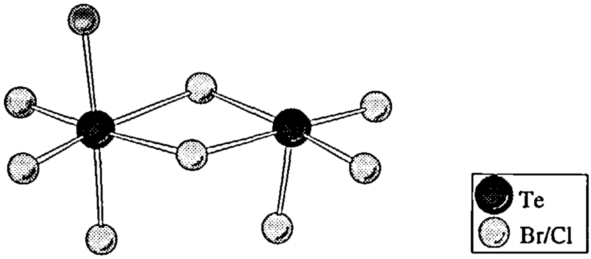
SYNTHESES

$[H_3O\cdot$(dibenzo-18-crown-6)]$[Te_2Br_9]$ (1) and $[H_5O_2\cdot$(bis-dibromo-dibenzo-24-crown-8)$]_2[Se_3Br_8]$ (3) were synthesized by adding the dibenzo crown ethers to solutions of the chalcogen tetrahalides in acetonitrile containing small amounts of concentrated hydrobromic acid. $[H_5O_2][Te_2Cl_9]\cdot 2C_4H_8O_2$ (2) crystallizes from a solution of $TeCl_4$ in 1,4-dioxane with small amounts of hydrochloric acid. Single crystals were obtained by careful cooling of the saturated solutions.

DESCRIPTION AND DISCUSSION OF THE STRUCTURES

Compound 1 crystallizes in the triclinic space group $P\bar{1}$ (a = 9.010(2) Å, b = 13.403(3) Å, c = 14.606(4) Å, α = 98.94(2)°, β = 100.40(2)°, γ = 91.40(2)° at 150 K). The dinuclear $[Te_2Br_9]^-$ anion can be described as a $TeBr_6$ octahedron and a $TeBr_5$ square pyramid sharing one edge. An additional weak η^6-interaction to a benzo group of the crown ether completes the $TeBr_5$ fragment to a highly distorted octahedron. The cationic unit in 1 consists of a crown ether-coordinated $[H_3O]^+$ ion. The C-O and C-C bond lengths of the crown ether are shorter than comparable distances in non-cyclic systems. This is known as the macrocyclic effect [4].

Compound 2 crystallizes in the orthorhombic space group Pnma (a = 17.023(4) Å, b = 13.389(4) Å, c = 10.900(3) Å at 150 K). The structure of the $[Te_2Cl_9]^-$ anion in 2 is analogous to the $[Te_2Br_9]^-$ anion in 1. In 2 the coordination sphere of the square pyramidal fragment is completed to a distorted octahedron by a weak interaction to an oxygen atom of the cationic $[H_5O_2]^+$ unit. Hydrogen bonds between the $[H_5O_2]^+$ units and 1,4-dioxane molecules connect the oxonium ions to a two-dimensional supramolecular network.

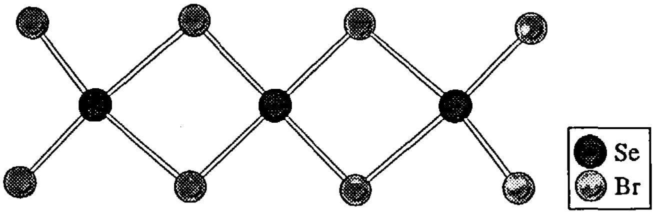


Structure of the $[Te_2X_9]^-$ anions (X = Cl, Br) in 1 and 2

Compound 3 crystallizes in the triclinic space group $P\bar{1}$ (a = 10.499(2) Å, b = 13.033(3) Å, c = 14.756(3) Å, α = 113.77(3)°, β = 98.17(3)°, γ = 93.55(3)° at 150 K). The trinuclear linear $[Se_3Br_8]^{2-}$

anion consists of three edge-sharing square planar $SeBr_4$ units. The terminal Se-Br bonds are significantly shorter than the bridging ones.

There is a strong correlation between bonds in linear X-A-X systems (A = Se, Te; X = Cl, Br) in all three structures. A short A-X bond increases the bond length on the other side of the X-A-X system. This „*trans* influence“ can be explained by the 3-center-4-electron model and is well known for halochalcogenates(II) and -(IV) [5].



Structure of the $[Se_3Br_8]^{2-}$ anion in 3

Acknowledgments

We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

References

[1] O. Reich, S. Hasche, K. Büscher, I. Beckmann and B. Krebs, *Z. Anorg. Allg. Chem.* **1996**, *622*, 1011
[2] S. Hasche, O. Reich, I. Beckmann and B. Krebs, *Z. Anorg. Allg. Chem.* **1997**, *623*, 724
[3] O. Reich and B. Krebs, *Z. Kristallogr. (Suppl.)* **1996**, *11*, 93
[4] N. D. Dalley, in *Synthetic Multidentate Macrocyclic Compounds* (eds.: R. M. Izatt, J. J. Christensen), Academic Press, New York, **1978**, pp 207
[5] B. Krebs and F.-P. Ahlers, *Adv. Inorg. Chem.* **1990**, *35*, 257