

UNCLASSIFIED

AD 4 4 1 2 4 1

DEFENSE DOCUMENTATION CENTER

FOR

SCIENTIFIC AND TECHNICAL INFORMATION

CAMERON STATION, ALEXANDRIA, VIRGINIA



UNCLASSIFIED

DISCLAIMER NOTICE

THIS DOCUMENT IS BEST QUALITY PRACTICABLE. THE COPY FURNISHED TO DTIC CONTAINED A SIGNIFICANT NUMBER OF PAGES WHICH DO NOT REPRODUCE LEGIBLY.

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

REPRODUCED BY DDC

AS DDC No. _____

441241

OFFICE OF NAVAL RESEARCH

Contract No. N. 62558-3589

Task No. NR. 356-445

TECHNICAL REPORT NO. 1

Four Coordinate Complexes of Carbon

by

R. N. Collings, R. S. Nyholm and M. L. Tobe

Prepared for publication

(In condensed form)

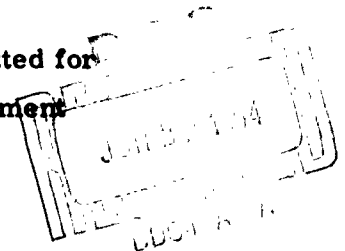
in "Nature"

University College London

Department of Chemistry

March 1964

Reproduction in whole or in part is permitted for
any purpose of the United States Government



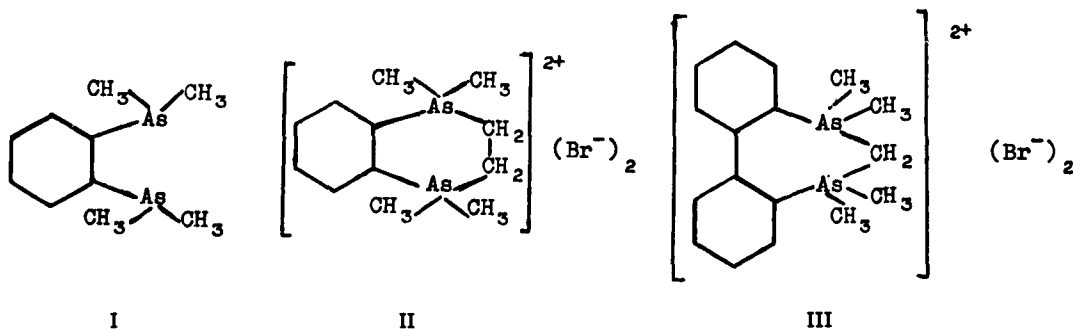
441241

FOUR COORDINATE COMPLEXES OF CARBON

1. INTRODUCTION

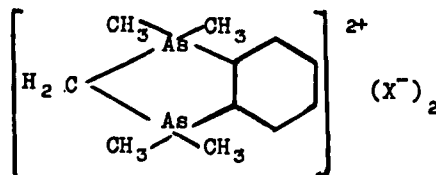
Studies in these laboratories of complexes formed by the $1s^2$ core (light) elements, beryllium and boron, with the ditertiary arsine, *o*-phenylene bis(dimethyl arsine) ^{1,2} (I) have now been extended to carbon.

Compounds of the type $[\text{CH}_3\text{AsR}_3]^+ \text{X}^-$ have been known for a long time and more recently ³ derivatives of the type II and III have also been described.



We have now developed this series to include complexes in which the same carbon is coordinated to two, three and four arsenic atoms; examples of the last two of these were previously unknown.

2. Di hydro (*o*-phenylenebisdimethyl arsine) carbon IV salts



Preparation:

(a) Bromide. Equimolar quantities of *o*-phenylene bisdimethyl arsine and dibromomethane were reacted and the yellow solid, on recrystallisation from methanol gave white crystals M. P. 220°.

Found C, 28.5, H, 4.3; As, 32.4; Br, 35.3%

$\text{C}_{11}\text{H}_{12}\text{As}_2\text{Br}_2$ requires C, 28.8; H, 3.9; As, 32.5; Br, 34.8%

Equivalent conductivity of 10^{-3}M aqueous solution = 250 mhos

(b) The iodide, M. P. 239° was prepared in an analogous way using diiodomethane.

Found C, 23.7; H, 2.9; I, 45.8%

$C_{11}H_{12}As_2I_2$ requires C, 23.8; H, 3.2; I, 45.8%

Equivalent conductivity of $10^{-3}M$ aqueous solution = 246 mhos

(c) The perchlorate was prepared by adding a hot saturated ethanolic solution of sodium perchlorate to a hot saturated ethanolic solution of the bromide. The perchlorate crystallised out on cooling as shiny white needles, M. P. 270°.

Found C, 26.7; H, 3.6; As, 30.0%

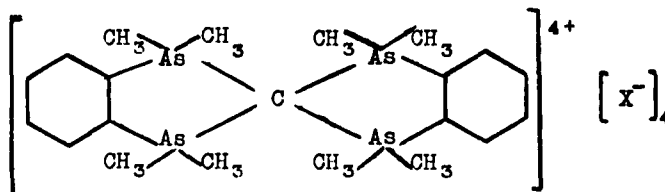
Calc. for $C_{11}H_{12}O_8As_2Cl_2$ C, 26.4; H, 3.6; As, 30.0%

Equivalent conductivity of $10^{-3}M$ aqueous solution = 202 mhos

PROPERTIES These complexes are stable white crystalline salts readily soluble in water and the halide ions are freely titrateable with silver nitrate. The conductivities correspond closely the values expected for 2 : 1 electrolytes.

It is possible to evaporate the aqueous solution and recover the complex unchanged.

3. bis (o-phenylenebisdimethyl arsine) carbon (IV) salts



Preparation:

The Bromide was obtained by reaction two moles of the diarsine with one mole of carbon tetrabromide. The solid reaction product was recrystallised from absolute ethanol/ether and the bromide obtained as white crystals M. P. 82°.

Found C, 28.0; H, 3.3; As, 30.0; Br, 35.6%

Calc. for $C_{21}H_{32}As_4Br_4$ C, 28.0; H, 3.6; As, 33.2; Br, 35.4%

The iodide was obtained in a similar way but using carbon tetraiodide and obtained as white crystals M. P. 231°.

Found C, 23.2; H, 2.9; As, 27.1; I, 46.9%

$C_{21}H_{32}As_4I_4$ requires C, 23.1; H, 3.0; As, 27.4; I, 46.5%

The perchlorate was prepared by mixing hot ethanolic solutions of the bromide and sodium perchlorate and crystallised out on cooling. M. P. 243°.

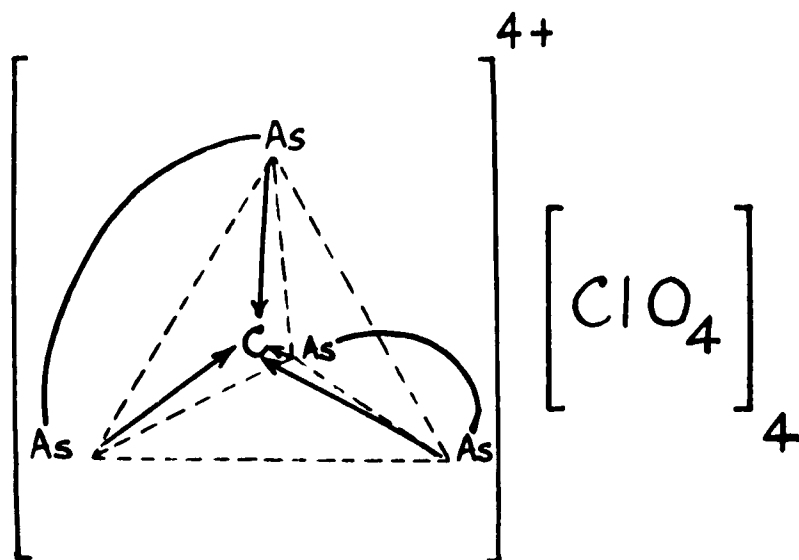
Found C, 26.3; H, 4.0; As, 30.7%

$C_{21}H_{32}O_{16}As_4Cl_4$ requires C, 25.7; H, 3.3; As, 30.5%

PROPERTIES These complexes are stable white crystalline solids that are extremely soluble in water. The bromide and iodide ions are readily titrateable and the conductivities indicate extensive ion association which is not unusual for ions bearing this high positive charge.

The low melting point of the bromide is of interest. It has been observed that, if the liquid is heated above 100° it appears to bubble and then resolidifies. The white solid formed does not remelt until the temperature is above 200°. The nature of this reaction is uncertain but similar degradations of quaternary arsonium halides, whereby methyl halide is evolved and the tertiary arsine formed are not uncommon. The infra-red spectra have been recorded.

4. DISCUSSION The unique feature of these new compounds is the number of quaternary arsenic atoms (or coordinate links) associated with the same carbon atom. Just as one can formulate complexes of metallic elements with four coordinate links e.g. the complex $[Zn(diamsine)_2](ClO_4)_2$ so the carbon compound can be written formally as shown in the figure. It is not suggested that there is any real distinction between the representation



BIS-*o*-phenylenebisdimethylarsine-carbon(IV)
tetra-perchlorate.

$R_3As^+ - C \rightleftharpoons$ and $R_3As \rightarrow \overset{+}{C} \rightleftharpoons$ but it is important to emphasise that no sharp distinction can be made between, say, Be(II) and C(IV) and that there is simply a gradual transition from Li(I) to C(IV) as the formal charge on the central atom increases.

We are now studying the reactions between $CHBr_3$, CHI_3 , CBr_4 and Cl_4 with a variety of tri and quadridentate arsine ligands, both with aliphatic and aromatic skeletons.

TECHNICAL REPORT DISTRIBUTION LIST

CONTRACTOR: University College London

NR NO.: 356-445

CONTRACT NUMBER: N6 2558-3589

	<u>No.</u> <u>Copies</u>			<u>No.</u> <u>Copies</u>
Commanding Officer Office of Naval Research Branch Office 230 N. Michigan Avenue Chicago 1, Illinois	(1)	U. S. Army Natick Laboratories Clothing & Organic Materials Division Natick, Massachusetts Attn: Associate Director	(1)	
Commanding Officer Office of Naval Research Branch Office 207 West 24th Street New York 11, New York	(1)	Harry Diamond Laboratories Washington 25, D. C. Attn: Library	(1)	
Commanding Officer Office of Naval Research Branch Office 1030 East Green Street Pasadena 1, California	(1)	Office, Chief of Research & Development Department of the Army Washington 25, D. C., Attn: Physical Sciences Division	(1)	
Commanding Officer Office of Naval Research Branch Office Box 39, Navy # 100, F. P. O. New York, New York	(7)	Chief, Bureau of Ships Department of the Navy Washington 25, D. C. Attn: Code 342A	(2)	
Director, Naval Research Laboratory Washington 25, D. C. Attn: Technical Information Officer Chemistry Division	(6) (2)	Technical Library, DLI-3 Bureau of Naval Weapons Department of the Navy Washington 25, D. C.	(4)	
Chief of Naval Research Department of the Navy Washington 25, D. C. Attn: Code 425	(2)	Defense Documentation Center Cameron Station Alexandria, Virginia	(20)	
DDR&E Technical Library Room 3C-128, The Pentagon Washington 25, D. C.	(1)	Commanding Officer U. S. Army Electronics Research and Development Laboratory Attn: SELRA/DR Fort Monmouth, New Jersey 07703	(1)	
Department of the Army Supply & Maintenance Command Maintenance Readiness Division Washington 25, D. C. Attn: Technical Director	(1)	Naval Radiological Defense Laboratory San Francisco 24, California, 94135 Attn: Technical Library	(1)	
Commanding Officer Army Research Office Box CM, Duke Station Durham, North Carolina Attn: CRD-AA-IP	(1)	Naval Ordnance Test Station China Lake, California Attn: Head, Chemistry Division	(1)	
		Aeronautical Systems Division ASRCNP Wright-Patterson AFB, Ohio	(1)	

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Atomic Energy Commission Division of Research Chemistry Programs Washington 25, D. C.	(1)	Dr William N. Lipscomb Department of Chemistry Harvard University Cambridge 38, Massachusetts	(1)
Atomic Energy Commission Division of Technical Information Extension Post Office Box 62 Oak Ridge, Tennessee	(1)	Mr W. M. Lee, Director Contract Research Department Pennsalt Chemicals Corporation 900 First Avenue King of Prussia, Pennsylvania	(2)
Commanding Officer U. S. Army Chemical Research and Development Laboratories Attn: Librarian Edgewood Arsenal, Maryland	(1)	Monsanto Research Corporation Everett Station Boston 49, Massachusetts Attn: Technical Library	(1)
Dr A. Eisenberg Department of Chemistry University of California Los Angeles, California	(1)	Dr T. L. Heying Organics Division Olin Mathieson Chemical Corporation 275 Winchester Avenue, New Haven, Connecticut	(1)
Dr P. A. Miller ONR Branch Office 1000 Geary Street San Francisco 9, California	(1)	New York Naval Shipyard Material Laboratory Brooklyn 1, New York Attn: Mr B. B. Simms	(1)
Dr Porter W. Erickson Chemistry Research Department Non-Metallic Materials Division Room 4-171 Naval Ordnance Laboratory White Oak, Silver Spring, Maryland	(1)	Naval Research Laboratory Washington 25, D. C. Attn: Dr R. B. Fox	(1)
Dr Albert Lightbody Naval Ordnance Laboratory White Oak, Silver Spring, Maryland	(1)	Dr M. E. Kenney Department of Chemistry Case Institute of Technology Cleveland, Ohio	(1)
Contracting Officer U. S. Navy Purchasing Officer 8 Rathbone Place, London W. 1, England	(1)	Dr J. C. Bailar, Jr. Department of Chemistry University of Illinois Urbana, Illinois	(1)
Director U. S. Navy European Research Contracts Program Navy # 100 Box 39 Fleet Post Office New York, New York	(1)	Dr A. B. Burg Department of Chemistry University of Southern California Los Angeles 7, California	(1)
Dr C. Haber Naval Ordnance Laboratory Corona, California	(1)	Dr R. Pepinsky Crystallographic Laboratory Department of Physics Pennsylvania State University University Park, Pennsylvania	(1)

	<u>No.</u> <u>Copies</u>	<u>No.</u> <u>Copies</u>
Dr A. L. Powell ONR Branch Office 495 Summer Street Boston 10, Massachusetts	(1)	Dr Riley Schaeffer Department of Chemistry Indiana University Bloomington, Indiana (1)
Dr E. G. Rochow Department of Chemistry Harvard University Cambridge 38, Massachusetts	(1)	Dr T. G. Fox Director of Research Mellon Institute 4400 Fifty Avenue Pittsburgh 13, Pennsylvania (1)
Dr T. D. Parsons Department of Chemistry Oregon State University Corvallis, Oregon	(1)	Dr P. D. George General Electric Company General Engineering Laboratory Schenectady, New York (1)
Dr A. V. Tobolsky Department of Chemistry Princeton University Princeton, New Jersey	(1)	Dr H. B. Jonassen Department of Chemistry Tulane University New Orleans 15, Louisiana (1)
Dr R. S. Stein Department of Chemistry University of Massachusetts Amherst, Massachusetts	(1)	Dr Henry Taube Department of Chemistry Stanford University Stanford, California (1)
Dr S. Young Tyree, Jr. Department of Chemistry University of North Carolina Chapel Hill, North Carolina	(1)	Dr H. Freiser Department of Chemistry University of Arizona Tucson, Arizona (1)
Dr A. M. Zwickel Department of Chemistry Clark University Worcester, Massachusetts	(1)	Dr R. N. Minne Science Department Culver Military Academy Culver, Indiana (1)
Dr M. M. Chamberlain Department of Chemistry Western Reserve University Cleveland, Ohio	(1)	Dr H. S. Gutowsky Department of Chemistry University of Illinois Urbana, Illinois (1)
Dr T. P. Onak Department of Chemistry Los Angeles State College Los Angeles, California	(1)	Dr W. S. Fyfe Department of Geology University of California Berkeley, California (1)
Dr D. C. Bradley Department of Chemistry University of Western Ontario London, Canada	(1)	