

Fig. 2.—Comparison of Raman spectra of potassium tantalate in solution with crystalline $K_8Ta_6O_{19} \cdot 16H_2O$. Left traces, double slit width; right traces, single slit width; all 10 cm.⁻¹. Top spectra (crystalline): sensitivity settings, 1 × 100RD4; period controls, left trace, 0.5; right trace, 0.3. Bottom spectra (solution): left trace sensitivity, 1.6 × 100RD4; period, 5.0; right trace sensitivity, 1 × 100RD4; period, 0.

likely that the lines at 170 and 145 cm.⁻¹ may not correspond to genuine vibrations for the tantalate ion. With our spectrometer spurious lines in this region are sometimes observed in the spectra of crystals, although in solution these lines, if observed at all, are usually much weaker. The close correspondence of the two spectra, with each of the seven lines (excluding 145 and 170 cm. $^{-1}$) observed in the solution having its counterpart in the solid within about 4 cm.⁻¹, strongly supports the conclusion that the same hexatantalate anions present in the crystal are also present in solution. The simplicity of the spectra, compared with those of less symmetrical ions (for example,¹⁰ $Mo_7O_{24}^{6-}$ provides further qualitative evidence for the octahedral arrangement of tantalum atoms proposed by Lindqvist. However, for the ion $Ta_6O_{19}^{8-}$ with O_h point group symmetry, there is a center of symmetry, which means there should be no coincidence between the Raman lines and infrared bands. The infrared spectrum of $K_8Ta_6O_{19} \cdot 16H_2O$ has been observed⁴ and one of the four bands (822 cm.⁻¹) has a frequency close to the 825 cm.⁻¹ Raman line. Our infrared measurements covering this region and below indicated lines at 843 (sharp), 694 (broad), 535 (medium), 402 (broad), and 355 (weak) cm.⁻¹. We checked the region of primary interest here with a Nujol mull, on a different instrument (Perkin-Elmer 221), with the preparation of potassium tantalate used in the Raman and ultracentrifugation work, and again found no indication of an 822 cm.⁻¹ line. We therefore believe the attribution of O_h point symmetry is correct, but in any case, our main conclusion, that the $Ta_{6}O_{19}^{8-}$ ion is present both in the solid and solution, is unaffected.

(10) J. Aveston, E. W. Anacker, and J. S. Johnson, Inorg. Chem., 3, 735 (1964).

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Isomerism in Some Boron and Boron-Carbon Frameworks

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The recent reports of an extensive derivative chemistry of some of the boron hydride anions¹ and the carboranes² have shown the desirability of a study of substitution isomers to be derived from the basic boron and boron-carbon frameworks of these compounds. The study of isomerism by group-theoretical methods is the most powerful and elegant method of attacking such a problem. Kennedy, McQuarrie, and Brubaker³ have recently given a new, pointgroup formulation and extensive discussion of the technique. Their paper should be consulted for details.

Calculations.—The determination of the number of geometrical isomers and enantiomorphic pairs was carried out by the method of Brubaker, et al., for substitution by one kind of substituent. The structures considered are $\mathrm{B}_{10}\mathrm{H}_{10}{}^{2-}\text{, }\mathrm{B}_{12}\mathrm{H}_{12}{}^{2-}\text{, and the three pos$ sible icosahedral dicarbaclovododecaborane(12) isomers. For the carboranes, calculations were carried out for substitution on all atoms and substitution on borons only. Cycle indices for each of these cases are given in Table I for both the point group of the molecule and its rotation subgroup. The total number of isomers and the number of geometric isomers for each of the structures are given in Table II. Note that as both 1,2- and 1,7-carborane⁴ have the same symmetry (C_{2v}) and are of the same degree (12, or 10 for borons only), the cycle indices and number of isomers are the same for both structures, although the isomers are completely different.

Discussion

The first communication on the susceptibility of the boron frameworks in $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ to electrophilic substitution¹ suggested that all isomers would not be formed in these reactions. For example, apical substitution in $B_{10}H_{10}^{2-}$ seemed to occur first, and this

⁽¹⁾ W. H. Knoth, H. C. Miller, D. C. England, G. W. Parshall, and E. L. Muetterties, J. Am. Chem. Soc., 84, 1056 (1962).

⁽²⁾ See e.g., H. Schroeder, T. L. Heying, and J. R. Reiner, Inorg. Chem., 2, 1092 (1963).

⁽³⁾ B. A. Kennedy, D. A. McQuarrie, and C. H. Brubaker, Jr., *ibid.*, **3**, 265 (1964).

⁽⁴⁾ These names will be used for brevity's sake to denote 1,2- and 1,7dicarbaclovododecaborane(12), and the 1,12 isomer will be named similarly.

TABLE I					TABLE III					
Cycle Indices					Isomers of $B_{10}H_{10-n}X_n^2$					
Parent molecule or ion	Point		Cycle index		_	Sub- stituted		Sub- stituted		Sub- stituted
	group	1/1610 1 6	•	4 1 4£57	n 1	atoms	n 4	atoms	n -	atoms
$B_{10}H_{10}^2$ -	${ m D}_4 { m D}_{4{ m d}}$		$f_{1^{2}f_{4^{2}}} + f_{1^{2}f_{2}}$ $2f_{1^{2}f_{4^{2}}} + f_{1^{2}f_{2}}$		1	$\frac{1}{2}$	4	-, ,-,	5	1,2,3,4,10
	1040	$4f_2f_8 + 4$		· ⊤ 4/2 ⊤		2		1,2,4,10 2,3,4,5		1,2,3,7,10 1,2,3,9,10
$B_{12}H_{12}^2 - I$		$\frac{1}{1} \frac{1}{60} [f_1^{12} + 24f_1^2 f_5^2 + 20f_3^4 + 15f_2^6]$						2,3,6,8		1,2,3,4,5
10124112	I_{h}			$f_{3}^{4} + 16f_{2}^{6} + 16$	2	1,10		1,2,3,9		1,6,7,8,9
	-11	· · ·	$24f_2f_{10} + 15f_1$	• • • • •	-	1,2		1,2,8,9		1,2,3,7,9
$1,2-C_2B_{10}H_{12}$	C_2	$\frac{1}{2}[f_1^{12} + f_2^6]$				1,6		1,6,7,8		1,2,4,6,7
$1,7-C_2B_{10}H_{12}$	C_{2v}	$\frac{1}{4}[f_1^{12} + f_2^6 + 2f_1^4f_2^4]$				2,3		1,2,3,4		1,2,4,6,9
$1,12-C_2B_{10}H_{12}$	D_5	$\frac{1}{10}[f_1^{10} + 4f_1^2f_5^2 + 5f_2^6]$			2,4		2,3,7,9		1,2,3,6,8	
	D_{5d}	$\frac{1}{20}[f_1^{10} + 4]$	$f_1^2 f_5^2 + 6 f_2^6$	$+ 4f_2f_{10} +$		$2,6^{a}$		1,2,3,7		2,3,4,5,6
		$5f_1 {}^4f_2 {}^4]$				$2,8^{a}$		1,2,6,7		2,3,4,6,9
$1,2-C_2B_{10}H_{12}$	C_2	$\frac{1}{2}[f_1^{10} + f$	2 ⁵]					$1,2,3,6^{a}$		2,3,4,7,8
$1,7-C_2B_{10}H_{12}$	C_{2v}	$\frac{1}{4}[f_1^{10} + f$	$f_{2^{5}} + f_{1^{2}}f_{2^{4}} +$	$f_1 {}^4f_2 {}^3]$				$1,2,4,6^{a}$		$1, 2, 3, 6, 10^a$
(borons					3	1,2,10		$1,2,7,8^{a}$		$1,2,4,6,10^{a}$
only)						1,2,3		$1,2,7,9^{a}$		$1,2,3,6,7^{a}$
$1,12-C_2B_{10}H_{12}$	$\mathrm{D}_{\mathfrak{d}}$	$\frac{1}{10}[f_1^{10} + d$				1,2,4		$1,2,6,10^{a}$		$1,2,3,4,7^{a}$
(borons	D_{5d}		$4f_{5^2} + 6f_{2^5}$	$+ 4f_{10} +$		1,6,7		$1,2,8,10^{a}$		$1,2,3,4,6^{a}$
only)		$5f_1^2f_2^4$]				1,6,8		$2,3,6,7^{a}$		$1,2,3,6,9^a$
						2,3,7		$2,4,6,8^{a}$		$1,2,4,6,8^{a}$
		TABLE II				2,3,9		$2,3,4,7^{a}$		$1,2,6,7,8^a$
Number	of Geom	ietrical and Optical Isomers				2,3,4		$2,3,4,6^{a}$		1,2,6,8,9ª
			Total	Geom.		$1,2,6^{a}$		$2,3,6,9^{a}$		$2,3,4,6,7^{a}$
		12	isomers	isomers ^a		$1,2,8^{a}$				$2,3,4,6,8^{a}$
$\mathbf{B}_{10}\mathbf{H}_{10-n}\mathbf{X}_n$		1	2	2		2,3,6ª				
		2	9	7		2,4,6ª				
		3	16	12	^a T	hese isomers	are on	e of an enantiom	orphic	pair.
		4	33	22						
		5	34	23				TABLE IV		
$\mathrm{B}_{12}\mathrm{H}_{12-n}\mathrm{X}_n$			1 1 1			Isomers of $B_{12}H_{12-n}X_n^{2}$				
		2	3	3		Sub-		Sub-	~	Sub-
		3	5	5		stituted		stituted		stituted
		4	12	10	n	atoms	п	atoms	п	atoms
		$\frac{5}{6}$	14	12	1	1	5	1,2,3,4,5	6	1,2,3,4,11,12
$1,2-C_2B_{10}H_{12-n}X_n$			$ \begin{array}{c} 24\\ 6 \end{array} $	$\frac{18}{5}$	_			1,2,3,4,7		1,7,8,9,10,11
$1, 2 - C_2 B_{10} H_{12-n} X_n$ $1, 7 - C_2 B_{10} H_{12-n} X_n$		$\frac{1}{2}$	36	3 23	2	1,2		1,2,3,4,12		1,2,5,8,10,12
(substitution on		2	110	65		1,7		1,2,3,5,12		1,2,3,4,6,8
all atoms)		4	250	143		1,12		1,7,8,9,10		1,2,3,7,9,12
an acoms)		5	$\frac{200}{396}$	218	0	1 0 10		1,2,3,10,11		$1,2,3,4,7,12^a$
		6	472	258	3	1,2,12		1,2,4,8,9		$1,2,3,4,5,7^{a}$
$1,12-C_2B_{10}H_{12-n}X_n$		1	2	208		1,2,3 1,2,4		1,2,3,5,7 1,2,4,7,10		$1,2,3,4,5,8^a$
(substitution on		2	10	8		1,2,4 1,7,8				$1,2,3,5,7,12^{a}$
all atoms)		3	22^{10}	16		1,7,8		1,2,4,11,12 1,2,4,8,10 ^a		$1,2,3,5,10,12^{a}$ $1,2,3,7,10,12^{a}$
an atoms,		4	57	37		1,1,0		$1,2,4,8,10^{\circ\circ}$ $1,2,3,5,10^{\circ}$		1,2,3,7,10,12"
		5	80	50			6	1,2,3,4,5,6		
		6	104	64	4	1,2,3,4	0	1,2,3,4,5,9		
$1,2-C_2B_{10}H_{12-n}X_n$		1	5	4		1,2,4,5		1,2,3,4,5,12		
$1,7-C_2B_{10}H_{12-n}X_n$		2	25	16		1,2,4,8		1,2,3,10,11,12		
(substitution on		3	60	35		1780		1005010		

 $\begin{array}{cccccc} 1,12-C_{2}B_{10}H_{12-n}X_{n} & 1 & 1 \\ (substitution on & 2 & 7 \\ borons only) & 3 & 12 \\ & & 4 & 26 \\ & & 5 & 26 \end{array}$

(substitution on

borons only)

^{*a*} The number of enantiomorphic pairs is given by the difference between the numbers of total isomers and of geometric isomers.

3

4

 $\mathbf{5}$

60

110

126

35

63

72

1

 $\mathbf{5}$

8

16

16

would be supposed to exert a directive influence on further substitutions. Such behavior had been expected on theoretical grounds.⁵ A fairly complete prediction of reactivities toward both electrophilic

(5) W. N. Lipscomb, A. R. Pitochelli, and M. F. Hawthorne, J. Am. Chem. Soc., 81, 5833 (1959).

^a These are one of an enantiomorphic pair.

1,7,8,9

1,7,8,10

1,2,4,12

1,2,3,12

1,2,10,12

 $1,2,7,12^{a}$

1,2,9,12ª

and nucleophilic reagents has been given by Hoffmann and Lipscomb for both the carboranes and the $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ ions.⁶

1,2,3,5,8,12

1,2,3,5,10,11

1,2,3,5,7,9

A more recent experimental paper⁷ suggests that, at

(6) R. Hoffmann and W. N. Lipscomb, J. Chem. Phys., 36, 3489 (1962); 37, 520 (1962).

(7) W. H. Knoth, H. C. Miller, J. C. Sauer, J. H. Balthis, Y. T. Chia, and E. L. Muetterties, Inorg. Chem., 3, 159 (1964).

least for halogenation reactions, the rates are comparable to collision rates, and random substitution seems to result. Hence a knowledge of the isomer possibilities seems even more important than would be the case if clear-cut directive influences were acting.

In Tables III and IV are shown all the possible isomers for $B_{10}H_{10-n}X_n^{2-}$ and $B_{12}H_{12-n}X_n^{2-}$. The numbering system is that employed by Muetterties, *et al.*⁷ Table IV gives, in effect, all of the possible permutations of two kinds of objects at the vertices of an icosahedron. All of the possible geometries of carborane derivatives are thus also included, although because of the nonequivalence of all vertices in those structures, each $B_{12}H_{12-n}X_n^{2-}$ isomer corresponds to several isomers of $B_{10}C_2H_{12-n}X_n$.

No explicit consideration has been given to isomerism among products containing more than one kind of substituent. The number of isomers is, of course, enormous. The number of isomers of $B_{12}H_{10-m}$. $X_mY_2^{2-}$ is implicit in the total of the isomers for the three carboranes, using boron substitution only. Thus there are 11 isomers for m = 1, 57 for m = 2, 132 for m = 3, 246 for m = 4, and 278 for m = 5.

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Observations on the Complex between Uranyl and Chlorite Ions

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Chlorite is known to be a good oxidizing agent in aqueous solution,¹ but very little is known about its ability to form complexes with metal ions. During the course of some experiments in which aqueous solutions of uranium(IV) were being oxidized by ClO_2^{-} , a transient yellow color was observed. This color has been interpreted in terms of a complex between UO_2^{2+} and ClO_2^{-} . The purpose of this report is to indicate the progress which has been made in studying the properties of this complex.

Experimental

In all of the measurements the quantity of interest was ΔA , the enhancement of absorbancy per cm. of cell length in the mixed acidic solutions of UO_2^{2+} and CIO_2^{-} compared to that on the basis of no interaction. Both UO_2^{2+} and CIO_2 , the decomposition product of CIO_2^{-} in acid solution, are yellow and absorb light in the same spectral region as the observed uranium chlorite complex. Therefore, in this region, where all three species are

absorbing, a blank solution containing each of these separately was run in the reference compartment vs. a cell containing the UO_2^{2+} -ClO₂⁻ mixture. The hydrogen ion concentration and the ionic strength (I = 1.00 M) were carefully matched in an attempt to minimize variation in activities. To effect changes in [H⁺] and [UO_2^{2+}], sodium perchlorate was substituted for these species. The reference cell with ClO₂⁻ contained Mg²⁺ in place of UO_2^{2+} to maintain similar ionic media in the two cells.

Although HClO₂ disproportionates fairly rapidly to form ClO₂, this reaction is much slower than the formation of the ClO_2^- complex. The rate law for the disproportionation reaction²

$$4HClO_2 = Cl^- + 2ClO_2 + ClO_3^- + 2H^+ + H_2O$$

reported by Barnett is^{2,3}

$$-d(HClO_2)/dt = k(HClO_2)^2$$

and the value of k at 25° is 1.4 l. mole⁻¹ min.⁻¹.

To minimize the effect of ClO_2 , the ClO_2^- solutions of the appropriate ionic strength were injected simultaneously into the acidic solution of UO_2^{2+} in the sample compartment and the solution of identical ionic strength and acidity containing Mg²⁺ substituted for $\mathrm{UO}_2{}^{2+}$ in the reference compartment. This rapid injection and mixing was achieved by the use of matched spring-loaded syringes. The tandem firing of these syringes was within 10 msec. and the mixing time is less than 30 msec.⁴ In this way the kinetic reaction of $C1O_2^-$ to form $C1O_2$, a species absorbing in the region of interest, was automatically subtracted from the observed spectra. By use of a reference cell containing UO_2^{2+} , simultaneous corrections were made for the uncomplexed UO_2^{2+} . The effect of Cl⁻ and ClO₃⁻ on the UO_2^{2+} spectrum was shown to be negligible. It was also shown that the slit width required to make this type of measurement was not large enough to introduce any errors.

Differences in zero time mixing were carefully checked by comparing blank solutions of perchloric acid into which ClO_2^- was injected in both sample and reference compartments. Perfect mixing and timing should result in no change of absorbance as a function of time in the region of absorption of ClO_2 . The blank experiments showed that the solutions could be matched to within 1% by this method. The spectra of the chlorite complex showed only very small changes with time, presumably due to errors in volume and zero time mixing, and none of the characteristics of the UO_2^{2+} or ClO_2 spectra was evident. Changes as small as 5% in the ClO_2^- concentration would have been detected as differences in rate of ClO_2 formation. Since differences of this type were not observed, it has been concluded that less than 5% of the ClO_2^- has been used in complex ion formation.

The analytical procedures used to determine the concentration of UO_2^{2+} , CIO_2^{-} , and $HCIO_4$ are the same as those described previously.^{1a} All measurements were made at 25° using a Cary Model 14M spectrophotometer with a thermostated cell compartment using 2-cm. quartz cells.

Results and Discussion

Due to the absorption of light by UO_2^{2+} and ClO_2 in the region of interest, the most meaningful data have been collected at 370 m μ , where these interferences could be minimized. These data are summarized in Table I.

The concentration of $[UO_2^{2^+}]$ and ΣClO_2^- given in Table I are the stoichiometric quantities of these species. The actual concentration of free ClO_2^- and H⁺ have been calculated from the equilibrium

$$\mathrm{HClO}_2 = \mathrm{H}^+ + \mathrm{ClO}_2^-$$

^{(1) (}a) D. M. H. Kern and G. Gordon, "Theory and Structure of Complex Compounds," B. Jezowska-Trzebiatowska, Ed., Pergamon Press, 1964, p. 655; (b) B. J. Fontana and W. M. Latimer, J. Am. Chem. Soc., 69, 2598 (1947).

⁽²⁾ H. Taube and H. Dodgen, ibid., 71, 330 (1949).

⁽³⁾ B. Barnett, Thesis, University of California, 1935.

⁽⁴⁾ R. Thompson and G. Gordon, J. Sci. Instr., submitted for publication.