

CarrierFree Radioisotopes from Cyclotron Targets. VI. Preparation and Isolation of Ag105,106,111 from Palladium

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The Crystal Structures of CeB_4 , ThB_4 , and UB_4

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January 9, 1950

THE compounds CeB_4 , ThB_4 , and UB_4 have been shown to crystallize in a new structure, which has been worked out from x-ray diffraction patterns. This structure is designated as the " UB_4 type structure," since that was the compound first observed. After the original preparation of this manuscript, we learned of the work of Andrieux,¹ who confirmed the identity of UB_4 by chemical analysis, and of Bertaut and Blum,² who found the unit cell dimensions and uranium coordinates for UB_4 crystals. They did not report the positions of the boron atoms. Their results are in agreement with ours reported here (with change of origin).

These borides were prepared by D. L. Sawyer and L. Brewer of this laboratory, who heated the metals and boron together in vacuum at about 1500°C. Powder diffraction patterns were obtained of the three compounds. Rotation and Weissenberg patterns were obtained for [110] and [001] axes of a small single crystal of ThB_4 . The patterns were indexed on tetragonal lattices whose dimensions are listed in Table I ($\text{CrK}\alpha_1 = 2.2896\text{\AA}$).

TABLE I. Lattice parameters.

	<i>a</i>	<i>c</i>	<i>c/a</i>	X-ray density
CeB_4	$7.205 \pm 0.008\text{\AA}$	$4.090 \pm 0.005\text{\AA}$	0.568	5.74 g/cm ³
ThB_4	7.256 ± 0.004	4.113 ± 0.002	0.567	8.45
UB_4	7.075 ± 0.004	3.979 ± 0.002	0.562	9.38 ^a
UB_4^b	7.066	3.97	0.562	

^a Andrieux (see reference 1) reports 9.32 as the experimental density.

^b Bertaut and Blum (see reference 2).

Consideration of the intensities leads to the following structure for the metal atoms:

$$\begin{aligned} &\text{Space group } D_{4h}^5 - P4/m\bar{b}m \\ &4 \text{ Ce, Th, U in } 4(g): \pm(u, 1/2+u, 0; 1/2-u, u, 0) \\ &u=0.31. \end{aligned}$$

These metal atoms are coplanar, with each having five nearly equidistant neighbors in the plane. Each metal atom has two neighbors in adjacent planes, but these are at a greater distance. This structure has holes, between the layers, which are best filled by boron atoms as follows:

$$\begin{aligned} &4 \text{ BI in } 4(e): \pm(0, 0, v; 1/2, 1/2, v) \\ &v=0.2 \\ &4 \text{ BII in } 4(h): \pm(w, 1/2+w, 1/2; 1/2-w, w, 1/2) \\ &w=0.1 \\ &8 \text{ BIII in } 8(j): \pm(x, y, 1/2; 1/2+x, 1/2-y, 1/2; y, x, 1/2; \\ &1/2+y, 1/2+x, 1/2) \\ &x=0.2 \\ &y=0.04 \end{aligned}$$

Thus the compounds were assigned formulas of the type MB_4 in agreement with the deduction, from the phases observed in various preparations, that the composition is between MB_2 and MB_6 .

This structure can be considered as a combination of two other more simple structures. Each atom BII is in a hole bounded by six metal atoms at corners of a triangular prism, as is the case with boron in the isostructural compounds AlB_2 ,³ ZrB_2 ,⁴ TiB_2 ,⁵ CrB_2 , NbB_2 , TaB_2 ,⁶ VB_2 ,⁷ and UB_2 .⁸ The atoms BI and BIII are grouped together as octahedra in holes bounded by metals at the corners of square prisms, analogous to the arrangement in the compounds CaB_6 , CeB_6 , ThB_6 , and others,⁹ in which a simple cubic array of metal atoms is interpenetrated by boron octahedra. The interatomic distances in the MB_4 compounds are in reasonable agreement with the corresponding ones in the MB_2 and MB_6 compounds.

A more detailed account of this work will be published subsequently. We are indebted to Professor Brewer and Mr. Sawyer for their cooperation in preparing the samples, to Mrs. Lee Jackson for taking the powder patterns, and to Mrs. Carol Dauben for some of the calculations. This research was supported by the United States AEC.

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Carrier-Free Radioisotopes from Cyclotron Targets. VI. Preparation and Isolation of $\text{Ag}^{105, 106, 111}$ from Palladium*

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January 23, 1950

RADIOACTIVE silver, produced by bombardment of palladium with 19-Mev deuterons, has been isolated without added isotopic carrier. Four long-lived radioisotopes of silver† are produced in a thick target by (*d*, *n*) and (*d*, 2*n*) reactions with deuterons of this energy: 45-day Ag^{106} , 8.2-day Ag^{106} , 225-day Ag^{110} , and 7.5-day Ag^{111} . Radioactive rhodium and radioactive ruthenium are also produced by (*n*, *p*) and (*n*, α) reactions respectively. The carrier-free radio-silver was separated from the target element and from the radioisotopes of rhodium and palladium by a precipitation technique using mercurous chloride as the co-precipitant.

A C.P. palladium metal target ($\frac{1}{4}$ in. Pd strip, soldered to a water-cooled copper plate with a silver-free hard solder) was bombarded with 19-Mev deuterons for a total of 200 $\mu\text{a-hr}$. at an average beam intensity of 20 μa . The irradiated surface was milled off (approximately 0.5 g of Pd) and dissolved in aqua regia. The solution was evaporated to dryness and dissolved in 500 ml of 0.5*N* HCl containing 50 mg each of rhodium and ruthenium hold-back carrier.

0.5 ml of a saturated solution of mercurous nitrate was added while the solution was stirred vigorously. The precipitate of Hg_2Cl_2 containing over 95 percent of the radio-silver was centrifuged, washed with 0.5*N* HCl and dissolved in a minimum volume of 16*N* HNO_3 . 200 mg of Na_2SO_4 were added and the solution was evaporated to dryness in a porcelain dish which was then heated to 450°C for two hours to drive off the mercury

carrier. The activity was quantitatively soluble in 10 ml of distilled water to give an isotonic saline solution of carrier-free radio-silver which was used in subsequent biological experiments.

The radio-silver was identified by half-life determinations, absorption measurements and by chemical separation with carrier. The decay was followed for 200 days and showed the approximately 8-day^{1,2} period of Ag¹⁰⁶,¹¹¹ and the 45-day³ period of Ag¹⁰⁶. One month after bombardment the activity showed only the 45-day period. After 150 days the decay curve began to level off, presumably into the 225-day⁴ period of Ag¹¹⁰; aluminum absorption measurements one week after bombardment showed the approximately 1.0-Mev beta-particle previously reported^{5,6} for Ag¹⁰⁶ and Ag¹¹¹; a tracer amount of activity added to a solution of Pd, Rh, Ru, and Ag in carrier amounts was quantitatively precipitated with the AgCl fraction.

We wish to thank the 60-inch cyclotron crew for the bombardments and target preparations, and Professor G. T. Seaborg for helpful suggestions.

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Absence of Spectroscopic Evidence for Rotational Isomerism in 2-Thiabutane*

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January 25, 1950

IN view of the recent unequivocal evidence^{1,2} for the existence of rotational isomers in normal butane it seems reasonable to expect similar behavior in similar small organic molecules. At the suggestion of Dr. H. M. Huffman of the United States Department of the Interior Bureau of Mines, Bartlesville, Oklahoma, we have investigated the Raman and infra-red spectrum of 2-thiabutane as a function of temperature.

The results of our experiments are conclusive in that they do not show the slightest evidence for the existence of two rotational isomers having an appreciable energy difference.

The relative intensity of lines in the Raman spectrum of the liquid remains strictly constant over a temperature range from 177° to 306°K. We have also investigated the infra-red spectrum of liquid and solid 2-thiabutane in the rocksalt region and find no change in the spectrum going from liquid to solid.

The sample furnished us by Dr. Huffman was stated to have an impurity of approximately 0.002 mole percent. In view of the fact that polarization data are lacking in the earlier work of Meyer³ we are including our measurements for the sake of completeness. In general, our results agree with those of Meyer. We did not obtain the 1098 cm⁻¹ frequency reported by him and with better resolution we have split the 1060 and 1430 frequencies into doublets. The Raman frequencies obtained are in cm⁻¹:

216 W.B.	Dep.	1042 M.	0.3
273 W.B.	0.5	1060 M.	0.3
355 S.	0.5	1259 W.	0.5
622 V.W.		1311 W.	0.5
656 V.V.S.	P.	1415 S.	
679 S.	P.	1429 S.B.	Dep.
727 V.S.	Dep.	2918 S.	P.
756 V.W.	Dep.	2922 S.	P.
975 M.B.	Dep.	3010 S.	Dep.

It should be mentioned that the infra-red spectrum of 2-thiabutane which we have obtained agrees in all particulars with the spectrum of this molecule obtained by the Bartlesville Laboratory of the U. S. Bureau of Mines.⁴ It is to be noted that most of the stronger Raman lines coincide with strong infra-red bands. A complete analysis of this spectrum must probably await further experimental data in the *KBr* region and correlation with the heat capacity data. This data has recently been obtained by Donald W. Scott of the Bartlesville Laboratory and will appear in a separate publication.

* This research was carried out on Contract N6onr-269, Task V, of the ONR.

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Hydrazine Formation in the Photolysis of Ammonia at 1849A, and in the Reaction of Ammonia with Hg 6(³P₁) and Hg 6(¹P₁) Atoms*

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January 6, 1950

SEVERAL investigators¹⁻³ have detected, as a product of the photolysis of ammonia, small amounts of a reducing substance which has been assumed to be hydrazine. However, only Gedye and Rideal⁴ have actually identified hydrazine in the products of the photolysis. In their method ammonia is distilled from a dry ice-acetone trap to a liquid air trap via a quartz reaction cell illuminated with a quartz mercury arc. Under these conditions they report a yield of approximately 0.7 cc of gaseous hydrazine in 125 minutes of irradiation, at a flow rate of about 80 cc per minute.

We have attempted to duplicate the results of Gedye and Rideal; but only trace quantities of hydrazine were obtained.

Since ammonia shows maximum absorption in the region of 1850A, we have undertaken studies of the photolysis of ammonia, in a fast-flow system, using the high energy resonance line of mercury at 1849A. For this purpose a special U-shaped mercury-rare gas resonance discharge tube was fabricated, using very thin optical quartz to obtain maximum transmission at 1849A. The lamp is di-chromatic, emitting both at 1849A and 2537A. The 2537 line is not absorbed by ammonia. Using ammonia as an actinometer, it was found that the light intensity at 1849A was 1-2×10⁻⁵ einstein per minute, depending upon the pressure of argon used in the lamp. The lamp was operated by a "neon sign" type transformer, with a 5000 v, 120 ma secondary. The electrodes of the lamp were ring-sealed into a large male quartz standard taper so that the lamp could be easily connected into the flow system.

In the fast-flow system ammonia is flowed past the resonance lamp, at atmospheric pressure, onto a cold finger trap containing dry-ice acetone, where it condenses, together with any hydrazine formed, and collects in a reservoir below. At the end of the run the liquid ammonia is evaporated to a small volume, after which water is added and the solution is acidified with concentrated hydrochloric acid. The amount of hydrazine formed is determined by titration with potassium iodate solution after the method developed by Penneman and Audrieth.⁵ Hydrazine was positively identified by characterizing the benzaldehyde derivative. Blank experiments, made by injecting a known amount of hydrazine into the ammonia stream, with the lamp turned off, showed that hydrazine recovery was quantitative.

In one run, made at a flow rate of 5 liters per minute, with the lamp operating at 355 volts and 119 milliamperes, 19 milligrams