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The Preparation and Structure of Lutetium Diboride, Scandium Dodecaboride and Lutetium Antimonide

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LuB_2 has been prepared by heating Lu_2O_3 and B at about 1500° . It has the AlB_2 structure with parameters $a_0 = 3.246 \pm 0.001 \text{ \AA}$. and $c_0 = 3.704 \pm 0.001 \text{ \AA}$. ScB_{12} , prepared by heating Sc_2O_3 and B, has the UB_{12} structure with a lattice parameter of $a_0 = 7.422 \pm 0.002 \text{ \AA}$. LuSb , prepared by heating the elements, has the NaCl structure with a lattice parameter of $a_0 = 6.0555 \pm 0.0003 \text{ \AA}$. The errors quoted here apply to the samples used and do not allow for the possible effects of impurities or non-stoichiometry in these samples. The reported existence of LuB_6 and ScB_6 could not be verified. Attempted preparations of these two compounds yielded mixtures of LuB_4 and LuB_{12} , and ScB_2 and ScB_{12} , respectively.

Introduction

The nuclear magnetic moment of Lu^{176} has recently been determined¹ by nuclear magnetic resonance in bulk samples. Because of the large nuclear quadrupole moment of this nuclide it was necessary to use compounds having cubic symmetry at the Lu atom to avoid broadening and shifting the nuclear resonance. Similar compounds of scandium and lanthanum were studied to evaluate possible shifts of the nuclear resonances.

Neshpor and Samsonov² reported that LuB_6 has the cubic CaB_6 structure, while Samsonov^{3,4} indicated that ScB_6 also has this structure. However, attempts to prepare these compounds for the n.m.r. work were unsuccessful. X-Ray studies of the Lu-B system were then undertaken which showed the presence of LuB_4 , LuB_{12} (which has also been prepared recently by La Placa, Binder and Post⁵) and LuB_2 which has not been reported before. The latter compound is one of the few examples of a rare-earth diboride. The scandium boride preparations were shown to consist of ScB_2 and a previously unreported compound, ScB_{12} .

Another possible cubic lutetium compound was suggested by Brixner's⁶ work on the paramagnetic rare-earth antimonides which have the NaCl structure. The compound LuSb subsequently was prepared and used in the n.m.r. studies.

Although the existence and stability of the transition-metal borides have been extensively studied, similar information for the rare-earth borides is somewhat limited. Samsonov³ has suggested that stable hexaborides are formed only by metals for which the first and second ionization potentials lie below certain values. For the dodecaborides La Placa, *et al.*,⁵ have noted that the metallic radius lies in a limited range. Muetterties⁷ has pointed out that the metals which yield borides of the form MB_n have a restricted range of values for their metallic radius and for the sum of their first and second ionization potentials, the range varying with n . These observations may be related, for, excluding the alkali metals, there is a rough reciprocal relation between the metallic radius and the sum of the two ionization potentials.⁸ It appears from the discussion of Lipscomb and Britton⁹ that each of the compounds MB_2 , MB_4 , MB_6 and MB_{12} requires the donation of two electrons per metal atom to form two- or three-dimensional covalent boron lattices.

(1) A. H. Reddoch and G. J. Ritter, *Phys. Rev.*, **126**, 1493 (1962).

(2) V. S. Neshpor and G. V. Samsonov, *Dopovidi Akad. Nauk Ukr. RSR*, **478** (1957).

(3) G. V. Samsonov, *Uspekhi Khim.*, **28**, 189 (1959).

(4) G. V. Samsonov, *Doklady Akad. Nauk SSSR*, **133**, 969 (1960).

(5) S. La Placa, I. Binder and B. Post, *J. Inorg. Nucl. Chem.*, **18**, 113 (1961).

(6) L. H. Brixner, *ibid.*, **15**, 199 (1960).

(7) E. L. Muetterties, *Z. Naturforsch.*, **12b**, 411 (1957).

(8) W. Finkelburg and W. Humbach, *Naturwissenschaften*, **42**, 35 (1955).

(9) W. N. Lipscomb and D. Britton, *J. Chem. Phys.*, **33**, 275 (1960).

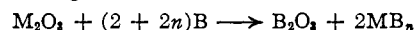
Such lattices would not be stable if the ionization energy of the two electrons were too great or if the metal atom were so large that it would strain the boron-boron bonds. The question of stability is probably complicated by other factors, however, such as metal-boron bonds and conduction electrons.

The present work provides some additional observations regarding the existence and structure of some borides.

Experimental

The samples were prepared from the following materials: Lu_2O_3 of 99% purity from American Potash and Chemical Co., Sc_2O_3 from A. D. MacKay Co., "amorphous, purified" boron from Fisher Scientific Co., antimony powder from British Drug Houses Ltd. and lutetium metal of at least 99% purity from Michigan Chemical Corp. Spectrographic analysis of these reagents gave the following approximate weight percentages for the major impurities: in Lu_2O_3 , 0.02% Ba and 0.01% Ca and Si; in Lu, 0.05% Fe and 0.04% Ni; in Sc_2O_3 , 0.5% Na and 0.1% Ca and Zr; in B, 5% Mg and 0.5% Si; and in Sb, 0.1% Fe and 0.02% Si.

The general procedure used for boride preparations was to heat a pressed pellet of metal oxide and boron *in vacuo*. Powders of boron and the appropriate oxide were mixed in stoichiometric amounts according to the reaction



although the reaction may actually yield¹⁰ BO rather than B_2O_3 . The pellet was placed in a small graphite oven, usually with excess boron between the pellet and the oven walls to avoid reactions with carbon. The excess boron was not used if the boron-to-metal ratio of the product was 2 or less. The system was evacuated to about 2 to 5×10^{-5} mm. pressure and the oven heated, by passing a current through its walls, to temperatures in the range 1350 – 1625° for periods from 5 minutes to 15 hours. The temperature rose to its final value in a couple of minutes and the pressure rose to roughly 5×10^{-2} mm. during this initial period. The samples were cooled to room temperature in less than 5 minutes. Temperatures were read with an optical pyrometer.

A few samples were prepared in the same manner as above using metal instead of oxide. One run was made using oxide and boron to which powdered graphite was added as a reducing agent. The products of these two methods were not significantly different from those obtained using oxide and boron.

Quantitative chemical analyses of the products were not made because most of the X-ray powder patterns showed the presence of two or more compounds. The stoichiometry of the initial mixture served as a guide to the products, but did not give precise information because of the possible loss of boron by volatilization and of the metal by reaction with the graphite oven or with the excess boron.

The LuSb sample was prepared by sealing a stoichiometric mixture of powdered Lu and Sb in an evacuated quartz tube and heating it at 750° for half an hour and then at 1000° for an hour and a half.

For X-ray exposures the powdered samples were mounted in thin-walled (0.01 mm.) soft-glass capillaries of 0.25 to 0.28 mm. diameter. A cylindrical camera of 114.6 mm. diameter was used with Ni-filtered Cu radiation ($\lambda(\text{CuK}\alpha_1) = 1.5405 \text{ \AA}$). A shrinkage correction was applied to all films used for final measurements. Whenever possible the $\text{K}\alpha_2$ lines were measured in addition to those given by the $\text{K}\alpha_1$ radiation and were used in the extrapolation techniques.

The intensities were estimated visually by comparison with a calibrated X-ray film strip having spots on a logarithmic scale.

(10) H. A. Eick and P. W. Gilles, *J. Am. Chem. Soc.*, **81**, 5030 (1959).

TABLE I
 DATA FOR LuB₂

<i>hkl</i>	<i>d</i> , Å., obsd.	<i>d</i> , Å., calcd.	<i>I</i> _{obsd.}	<i>I</i> _{calcd.}
001	3.656	3.704	26	22
100	2.781	2.811	59	57
101	2.222	2.239	100	100
002	1.840	1.852	9	13
110	1.614	1.623	32	30
102	1.539	1.546	38	44
111	1.478	1.486	38	37
200	1.398	1.406	18	18
201	1.308	1.314	38	36
003	1.230	1.235	6	4
112	1.217	1.220	32	34
103	1.128	1.130	26	27
202	1.117	1.120	35*	23
210	1.060	1.062	53*	22
211	1.020	1.021	71*	50
113	0.9813	0.9826	22	19
300	.9357	.9370	18	14
203	.9268	.9276	35	26
212	.9205	.9216	53	44
301	.9074	.9084	31	21
104	.8788	.8795	26	25
302	.8356	.8361	44	39
213	.8052	.8053	88	98
221	.7924	.7927	48	49

In the case of $K\alpha_1$ and α_2 doublets only the intensities of the $K\alpha_1$ lines are given, with the exception of the observed values for the LuB₂ pattern (Table I), which include the $K\alpha_2$ contribution.

Results and Discussion

Lutetium Diboride Structure.—A sample of LuB₄, prepared to aid in the analysis of the products of attempted LuB₆ preparations, showed extra X-ray lines of another phase, which was shown to be LuB₂. This new diboride was then found in a number of preparations having a low boron content.

The sample used for the final X-ray measurements was prepared from boron and oxide to yield a product with an atomic ratio B/Lu = 1. After heating without excess boron for 1.75 hr. at about 1500°, the X-ray powder pattern showed the product to contain LuB₄ and unreacted Lu₂O₃. However, when this sample was heated for an additional 5 hr. at about 1600°, it was found to contain LuB₂ and some Lu₂O₃. The tetraboride appeared to have completely reacted with the oxide to form diboride.

The diboride lines in the powder patterns were distinguished from those of the oxide by comparison with a film obtained with a pure sample of Lu₂O₃. Only three LuB₂ lines, marked by asterisks in Table I, were found to overlap those of Lu₂O₃. The diboride was first identified by comparison with the powder data of Jones and Marsh¹¹ for MgB₂, which is well suited for this purpose because its *c/a* ratio, 1.142, is almost identical with that of the lutetium compound, 1.141. The indexing of the lines was checked using the Bunn chart for hexagonal crystals.

The unit-cell parameters were refined by three cycles, which involved calculating the *a*- and *c*-values for the most suitable lines, plotting¹² them against $1/2(\cos^2 \theta / \sin \theta + \cos^2 \theta / \theta)$ and extrapolating to $\theta = 90^\circ$. The final unit-cell dimensions are $a_0 = 3.246 \pm 0.001$ Å., $c_0 = 3.704 \pm 0.001$ Å., $c/a = 1.141$.

These limits of error do not allow for the effect of impurities or non-stoichiometry in the sample. Various studies¹³⁻¹⁵ of diborides have shown that these factors

may shift the lattice parameters by amounts ranging from undetectable up to a few hundredths of an Ångström. In the present work samples of LuB₂ having excess Lu₂O₃ showed no differences, within an accuracy of 0.003 Å., from those having an excess of LuB₄. Although there was several per cent of Mg in the boron used to prepare the sample, spectrographic analysis showed less than 0.01% Mg in the LuB₂. The major impurities in the boride were Ag and Si in the 0.01% to 0.1% range. It may be concluded that the parameters given for LuB₂ are probably accurate to within 0.005 Å.

The interplanar spacings, *d*, calculated using the above parameters and given in Table I, compare well with the observed values. The calculated density, $\rho = 1.6602(\Sigma A/V)$, where ΣA is the sum of the atomic weights of the atoms in the unit cell and *V* is the volume of the unit cell in Å.³, was found to be 9.76 g. cm.⁻³.

Further confirmation of the identity of the LuB₂ was obtained by calculating the expected intensities of the powder pattern lines. The data reported for AlB₂,¹⁶ MgB₂¹¹ and MnB₂¹⁷ are of limited value because the metal atoms of these compounds are much lighter and thus could not be used for comparison.

The space group was taken to be P6/mmm(*D*_{6h}¹). The lutetium atom was placed at the origin and the boron atoms at ($1/3, 2/3, 1/2$) and ($2/3, 1/3, 1/2$). The scattering curve for lutetium was taken from the table published by Thomas and Umeda,¹⁸ and for boron from the data given by Ibers.¹⁹ Both sets of atomic scattering factors were corrected by the temperature factor $B = 1.5$ Å.². The absorption corrections were taken from the "International Tables for X-ray Crystallography,"²⁰ taking $\mu R = 13.0$.

The calculated *F*² values were also multiplied by the appropriate Lorentz, polarization and multiplicity factors and by an arbitrary scaling factor to bring them to the scale of the observed values. The results, which show a good agreement between the calculated and observed values, are given in Table I. The observed intensities marked with an asterisk are high because of the overlapping with Lu₂O₃ lines.

Correlation with Other Diborides.—In Fig. 1 the parameters of LuB₂ are plotted along with those of other diborides. (Unless other references are given, lattice parameters are selected from the compilations of Pearson¹⁴ and Gschneidner,²¹ while the metallic radii of Sc, Y and the lanthanides are taken from Gschneidner²¹ and those of other metals from Wells.²² The data for MnB₂ are given by Binder and Post.¹⁷) It can be seen that for the majority of compounds the relation between the lattice parameters and the metallic radius may be taken as linear within an accuracy of 0.05 Å. The LuB₂ parameters conform well to the empirical relationship.

While the diboride unit cell might be expected to increase with increasing metal-atom size, a linear relation might not have been anticipated. A simple model consisting of two-dimensional covalent boron networks

(13) J. M. Leitnaker, "Thermodynamic Properties of Refractory Borides," USAEC Report LA 2402.

(14) W. B. Pearson, "Handbook of Lattice Spacings and Structures of Metals," Pergamon Press, New York, N. Y., 1958.

(15) B. Post, F. W. Glaser and D. Moskowitz, *Acta Metallurg.*, **2**, 20 (1954).

(16) E. J. Felton, *J. Am. Chem. Soc.*, **78**, 5977 (1956).

(17) I. Binder and B. Post, *Acta Cryst.*, **13**, 356 (1960).

(18) L. H. Thomas and K. Umeda, *J. Chem. Phys.*, **26**, 293 (1957).

(19) J. A. Ibers, *Acta Cryst.*, **10**, 86 (1957).

(20) "International Tables for X-ray Crystallography," Vol. II, The Kynoch Press, 1959, p. 296.

(21) K. A. Gschneidner, "Rare Earth Alloys," D. Van Nostrand Co., Inc., New York, N. Y., 1961.

(22) A. F. Wells, "Structural Inorganic Chemistry," 3rd Ed., Oxford University Press, New York, N. Y., 1962.

(11) M. E. Jones and R. E. Marsh, *J. Am. Chem. Soc.*, **76**, 1434 (1954).

(12) J. B. Nelson and D. P. Riley, *Proc. Phys. Soc. (London)*, **57**, 160 (1945)

and rigid metal atoms would lead to a constant a -parameter of 3.02 Å. unless the metallic radius exceeded 1.51 Å. For larger metal atoms the a -parameter would be determined by metal-metal contacts and would be twice the metallic radius. Similar considerations would yield three segments in the graph of the c -parameters. However, such a model is undoubtedly too simple.

Uranium and plutonium²³ diborides lie above the lines. However, the other uranium borides, UB_4 and UB_{12} , and the other plutonium borides,²³ PuB_4 and PuB_6 , also lie above similar lines in the appropriate graphs. In these compounds U and Pu behave as metals with radii of 1.75 to 1.80 Å. It is difficult to comment on gold,²⁴ osmium²⁵ and ruthenium,²⁵ which also deviate from the lines although it is interesting that these metals, with silver,²⁴ have appreciably greater ionization potentials than do the other metals which yield diborides. Recently Aronsson, Stenberg and Åselius²⁶ have expressed some doubt about the structure of RuB_2 and OsB_2 .

Two quite different sets of values have been reported for YB_2 , one lying close to the lines, the other above them. The parameters for GdB_2 lie above the lines close to the higher values for YB_2 . Binder, who reported²⁷ the higher values for YB_2 , has subsequently suggested²⁸ that they apply to a "ternary boroxide or oxyboride." No details have been published for GdB_2 . It is interesting to note that the c/a ratios for the two sets of YB_2 data and for GdB_2 are identical, 1.16, and close to that for DyB_2 , 1.16, and LuB_2 , 1.14.

While the reason for apparent anomalies in YB_2 and GdB_2 remains to be determined, it appears that Lu along with Dy forms a diboride similar to that of other metals. It is not clear whether the absence of other lanthanide diborides reflects a lack of investigation or a physical factor causing instability. The work of Johnson and Daane²⁹ indicates that lanthanum does not form a diboride. If other lanthanide diborides do not exist the instability might be the result of the large size of the metal atoms, but it could hardly be caused by the magnitude of the ionization potentials since most metals forming diborides have larger potentials than do the lanthanides.

Scandium Dodecaboride.—Scandium dodecaboride was found in a number of samples prepared by heating Sc_2O_3 and B mixtures, designed to yield atomic ratios of B/Sc from 6 to 20, for 0.5 hr. to 2 hr. at various temperatures from 1350 to 1550°. However, the sample used for the final X-ray measurements was obtained by heating for an additional 8 hr. at 1550°, a product which contained ScB_2 and a small amount of Sc_2O_3 . This product had been obtained by heating a mixture of boron and oxide, designed to yield an atomic ratio of B/Sc = 6, for 10 minutes at about 1325°. The diboride lost scandium on prolonged heating, yielding the dodecaboride.

The film used for final measurements of ScB_{12} showed additional lines due to the presence of ScB_2 and of a very small amount of unknown material. The ScB_2 structure was identified by calculating the $\sin^2 \theta$ values using the parameters reported by Zhuravlev and Stepanova,³⁰ which agreed very well with the observed values. The ScB_{12} pattern was identified by analogy with UB_{12} ,³¹ ZrB_{12} ³² and TmB_{12} ⁵; YB_{12} was also pre-

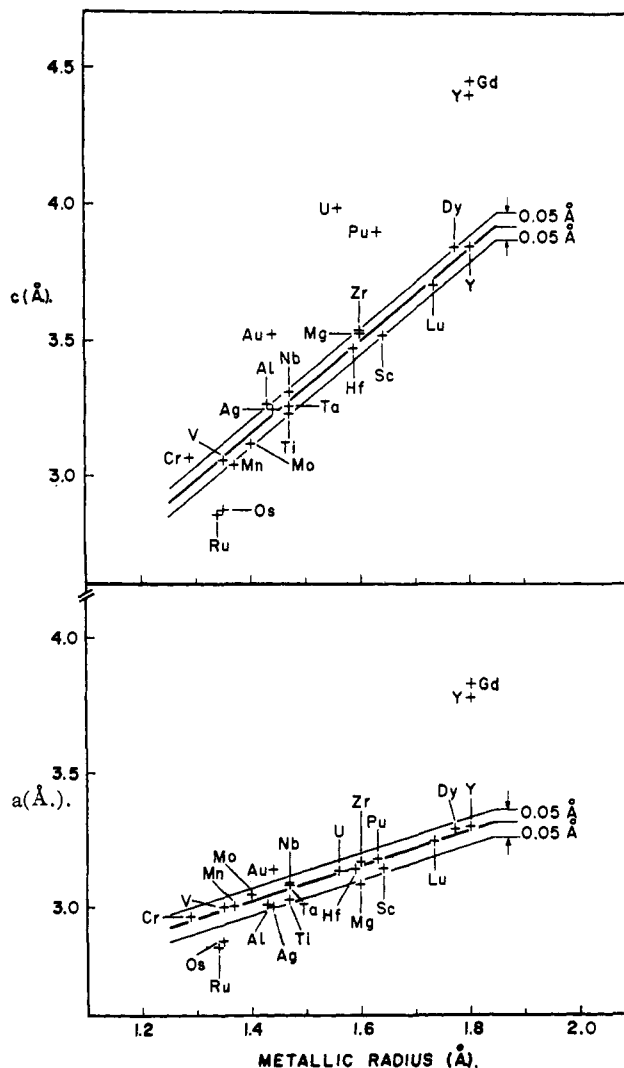


Fig. 1.—The lattice parameters of the diborides as a function of the metallic radius.

pared and its powder pattern was found very useful. Four lines, which are marked by asterisks in Table II, were found to be overlapping with the ScB_2 lines, causing their intensities to be too high.

TABLE II
DATA FOR ScB_{12}

hkl	d , Å.	I	hkl	d , Å.	I
111	4.221	18	711/551	1.037	5
200	3.662	22	640	1.028	10*
220	2.603	10	642	0.9902	1
311	2.223	50	731/553	.9650	12
222	2.139	100*	733	.9055	4*
400	1.844	9	820/644	.8998	2
331	1.693	12	822/660	.8742	7
420	1.651	6	751/555	.8565	4
422	1.508	14	662	.8510	4
511/333	1.422	3	840	.8297	2
440	1.306	3	911/753	.8146	9
531	1.251	14	842	.8096	6
600/442	1.233	12	664	.7910	3
620	1.170	30*	931	.7778	6
533	1.129	4			
622	1.116	2			

The structure of ScB_{12} is face-centered cubic. Extrapolation¹² of the a -values calculated for each line

(23) B. J. McDonald and W. J. Stuart, *Acta Cryst.*, **13**, 447 (1960).

(24) W. Obrowski, *Naturwissenschaften*, **48**, 428 (1961).

(25) C. P. Kempton and R. J. Fries, *J. Chem. Phys.*, **34**, 1994 (1961).

(26) B. Aronsson, E. Stenberg and J. Åselius, *Nature*, **195**, 377 (1962).

(27) I. Binder, *Powder Metall. Bull.*, **7**, 74 (1956).

(28) I. Binder, *J. Am. Ceram. Soc.*, **43**, 287 (1960).

(29) R. W. Johnson and A. H. Daane, *J. Phys. Chem.*, **65**, 909 (1961).

(30) N. N. Zhuravlev and A. A. Stepanova, *Kristallografiya*, **3**, 83 (1958).

(31) P. Blum and F. Bertaut, *Acta Cryst.*, **7**, 81 (1954).

(32) B. Post and F. W. Glaser, *J. Metals*, **4**, 631 (1952).

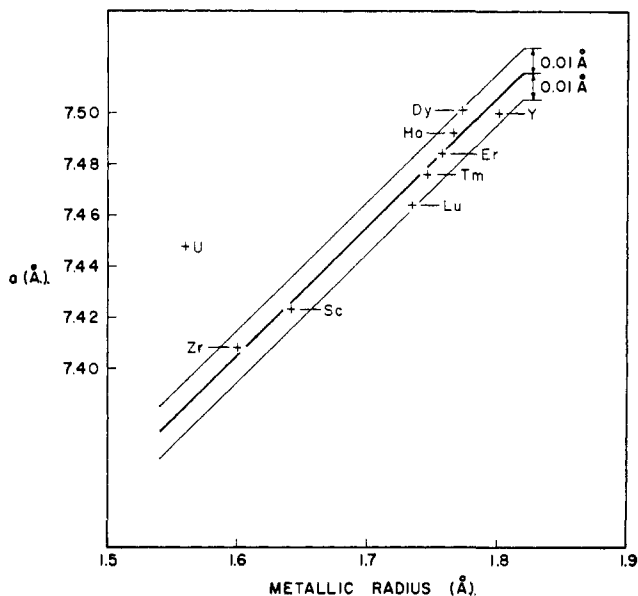


Fig. 2.—The lattice parameters of the dodecaborides as a function of the metallic radius.

yielded a parameter of $a_0 = 7.422 \pm 0.002 \text{ \AA}$. Again the limit of error does not allow for possible impurities or non-stoichiometry. Spectrographic analysis showed the major impurities in the sample to be Sr and Zr in the 0.1% to 1.0% range. No studies of the effects of impurities or non-stoichiometry on a dodecaboride lattice have been reported, although there are several such studies^{10,31,33} for the hexaboride lattice which may be relevant since both lattices consist of three-dimensional covalent boron networks. On the basis of these latter studies 0.005 Å seems to be a reasonable limit of error for the lattice parameter of ScB_{12} given above.

La Placa, Binder and Post⁵ give data for the dodecaborides of some rare earths and Y, as well as the previously known Zr and U compounds. These are shown in Fig. 2 along with the present value for ScB_{12} . Again, excluding uranium, the relation between lattice parameter and metallic radius may be taken as linear, the points falling within 0.01 Å of the line. As in the case of the diborides a model of rigid metal atoms and a covalent boron network would suggest a more complex relationship.

LaPlaca, Binder and Post⁵ have suggested upper and lower limits to the size of the metals forming dodecaborides. Specifically, they place Zr near the lower limit because of the failure to prepare HfB_{12} . As suggested in the Introduction, the lower limit to the metal atom size may in fact reflect an upper limit to the ionization potentials of the metal. This factor would more readily explain the difference between Zr and Hf for, while the metallic radii differ by only 0.01 Å, the sums of the first two ionization potentials⁸ are 19.97 and 21.9 e.v., respectively. Scandium is close to this limit with the corresponding sum of 19.34 e.v. It is surprising that La Placa, *et al.*,⁵ were unable to prepare ScB_{12} since their methods were very similar to those used here. It may be that the conditions for preparation are somewhat critical because Sc is near the limit of stability.

Lutetium Antimonide.—The structure of LuSb was identified by comparison with the data published by Brixner⁶ for the antimonides of other heavy lanthanides having the NaCl structure. The a -values, which were

(33) E. J. Felton, I. Binder and B. Post, *J. Am. Chem. Soc.*, **80**, 3479 (1958).

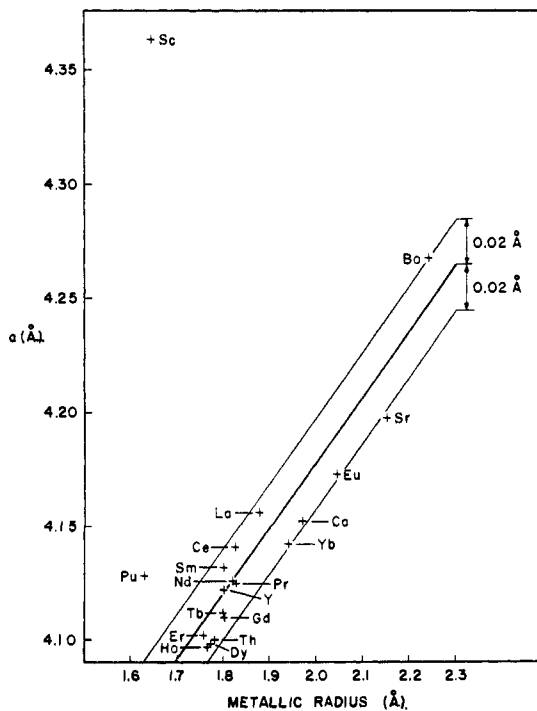


Fig. 3.—The lattice parameters of the hexaborides as a function of the metallic radius. The symbols of Th and Tb should be interchanged.

calculated for all the lines listed in Table III, gave an extrapolated¹² value of $a_0 = 6.0555 \pm 0.0003 \text{ \AA}$ for the lattice parameter of LuSb . There seems to be no useful information with which to estimate the possible error caused by impurities or non-stoichiometry. Such an error could be much larger than the one given above. The lattice parameter compares well with those given by Brixner for the other lanthanide antimonides, excluding ytterbium which is anomalous.

TABLE III
DATA FOR LuSb

hkl	$d, \text{ \AA}$	I	hkl	$d, \text{ \AA}$	I
200	2.998	100	600/442	1.008	42
220	2.127	100	620	0.9563	33
222	1.738	42	622	.9121	33
400	1.508	25	444	.8735	17
420	1.349	67	640	.8394	30
422	1.233	53	642	.8090	47
440	1.069	22			

Notes on the Existence of Lutetium and Scandium Hexaborides.—Although LuB_6 with the CaB_6 structure and a lattice constant of 4.11 Å has been reported by Neshpor and Samsonov,² no evidence of it was found in the present work. A total of 22 lutetium boride samples were examined. The mixtures of Lu_2O_3 and B were designed to yield products having B/Lu atomic ratios from 0 to 18 and were heated to various temperatures from 1400 to 1625° for periods from 5 min. to 15 hours. A few samples were prepared from metal and boron.

The X-ray results showed that almost every sample contained some LuB_4 . Compositions from B/Lu = 6 to B/Lu = 18 also contained LuB_{12} , while those from B/Lu = 1 to B/Lu = 4 contained LuB_2 . Unreacted Lu_2O_3 was found in most compositions having B/Lu ≤ 2 .

These results suggest that, if LuB_6 exists, it is not stable under the conditions used here, *i.e.*, preparation at 1400 to 1600°. The only evidence for the existence of LuB_6 is that of Neshpor and Samsonov.² They de-

scribe their sample as a mixture of LuB_4 and LuB_6 . Of the 15 lines of their powder pattern attributed to LuB_6 only two do not coincide with their LuB_4 lines. Comparison of their powder pattern with that of a pure sample of LuB_4 prepared here and with the lattice constants of LuB_4 given by Stepanova and Zhuravlev³⁴ indicates that all their lines came from the tetraboride.

Samsonov has reported the preparation of ScB_6 with the CaB_6 structure. Of the two different lattice constants for ScB_6 found in his papers,^{3,4} 4.355 kX. and 4.435 Å., the latter appears to be a misprint because in the paper in which it occurs the metal-metal distance is given as 4.35 Å.

In nine scandium boride samples prepared in the present work no ScB_6 was observed, the products consisting of ScB_2 and ScB_{12} . The samples were prepared from mixtures of oxide and boron designed to yield products ranging from B/Sc = 6 to B/Sc = 20. They were heated from half an hour to two hours at various temperatures from 1350 to 1550°. Samsonov³ stated that the ScB_6 appeared in a ScB_2 sample which had been heated for 9 to 10 hours as a cathode for thermionic emission studies. In the present work a ScB_2 sample

(34) A. A. Stepanova and N. N. Zhuravlev, *Kristallografiya*, **3**, 94 (1958).

containing some Sc_2O_3 was heated for 8 hr. *in vacuo*. The new lines which appeared in the X-ray powder pattern were those of ScB_{12} . An additional 8-hr. heating produced no significant change.

In Fig. 3 the lattice constants of the hexaborides derived from the more precise values in the literature^{14,21} are plotted against the metallic radii. (The data for Ca and La are those of Johnson and Daane.²⁹) Samsonov's³ value of 4.364 Å. (= 4.355 kX.) for ScB_6 appears to be remarkably large for such a small atom.

It seems that LuB_6 and ScB_6 are unstable and may not exist, thus marking the end of the range of stable hexaborides. In this connection, it is of interest that no metals with smaller radii or larger first and second ionization potentials than Sc and Lu are reported to form hexaborides. In addition, while the larger lanthanides such as La, Pr, Sm, Eu and Yb yield pure hexaborides, the smaller ones usually produce mixtures with tetraborides.

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[CONTRIBUTION FROM THE ISTITUTO DI CHIMICA GENERALE E INORGANICA, UNIVERSITA DI FIRENZE, FIRENZE, ITALY]

The Existence of Tetrahedral α -Branched Bis-(R-N-salicylaldimino)-nickel(II) Chelates

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X-Ray analysis and reflectance spectra data of some solid α -branched bis-(R-N-salicylaldimino)-nickel(II) complexes indicate that the open chain paramagnetic complexes (R = *i*-propyl, *s*-butyl and *t*-butyl) have an essentially tetrahedral structure, whereas the closed chain diamagnetic complexes (R = cyclopentyl, cyclohexyl and cyclooctyl) have a planar structure. Cryoscopic measurements on these compounds show that solute association is responsible for only a part of the paramagnetism exhibited by all of these complexes when dissolved in inert solvents. Furthermore, while the association becomes almost zero in boiling benzene, the percentage of paramagnetic forms in benzene, *m*-xylene and dibenzyl, as calculated by magnetic measurements, increases steadily with an increase in temperature from 20 to 180°. Spectrophotometric and dielectric polarization data of solutions of these complexes in inert solvents show that a high percentage of the observed paramagnetism results from tetrahedral species in equilibrium with the associated and the planar species. In this conformational equilibrium, the percentage of tetrahedral forms increases with increasing temperature.

Introduction

The existence of tetrahedral species in solutions of bis-(N-methylsalicylaldimino)-nickel(II) put forward¹ to account for the partial solution paramagnetism in inert solvents of this chelate was rejected on the basis of dipole moment measurements.² Later this compound was found to form a buff colored insoluble isomer.³ This isomer was the first example of a paramagnetic solid compound of the type bis-(salicylaldimino)-nickel(II). Its paramagnetism was attributed to an octahedral structure achieved by intermolecular association in the solid.³

This hypothesis was used by Holm to explain both the solution paramagnetism of the diamagnetic N-methyl complex and the paramagnetism of some α -branched complexes both in solutions of inert solvents and in the solid state.⁴

An X-ray analysis of the *i*-propyl and *s*-butyl-N-salicylaldimino-nickel(II) chelates showed them not to

be polymeric in the solid state but to have instead a tetrahedral structure.⁵ Cryoscopic and ebullioscopic measurements on solutions of these and other α -branched complexes can account for only a part of the solution paramagnetism instead of all of it as was originally suggested.⁴

These findings make it clear that further study on these systems is necessary. This paper reports the investigations of some α -branched nickel(II) complexes by means of magnetic, spectrophotometric, molecular weight and dipole moment measurements with the aim of elucidating the stereochemistry of these compounds in solutions of non-coordinating solvents.

Experimental

Preparation of Compounds. Nickel(II).—The bis-N-cyclopentyl, bis-N-cyclohexyl-, and bis-(N-cyclooctylsalicylaldimino)-nickel(II) complexes were prepared by refluxing 0.01 mole of bis-salicylaldehydonickel(II) dihydrate with a solution of 0.022 mole of the appropriate amine in 50 ml. of ethanol until the precipitate appeared homogeneous under a microscope. After cooling, the solid was collected on a filter and recrystallized from hot xylene. Green needles resulted which are slightly soluble in chloroform and benzene, and insoluble in petroleum ether.

Bis-(N-cyclopentylsalicylaldimino)-nickel(II).—m.p. 162–163°. *Anal.* Calcd for $\text{C}_{24}\text{H}_{28}\text{O}_2\text{N}_2\text{Ni}$: N, 6.44; Ni, 13.49. Found: N, 6.51; Ni, 13.37.

Bis-(N-cyclohexylsalicylaldimino)-nickel(II).—m.p. 213–215°. *Anal.* Calcd. for $\text{C}_{26}\text{H}_{30}\text{O}_2\text{N}_2\text{Ni}$: N, 6.05; Ni, 12.67. Found: N, 6.15; Ni, 12.60.

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