A sample of pentaborane obtained from the Mathieson Chemical Co. was fractionated in a high vacuum line and then distilled directly into the densitometer. The vapor pressure of 65–66 mm. at 0° agrees well with the literature value[5] of 66 mm. The infrared spectrum showed only the bands expected for pentaborane. The densitometer was sealed off, the weight of the liquid obtained, and the entire tube submerged in a well stirred low temperature bath. A calibrated copper–constantan thermocouple was placed directly against the bulb of the densitometer. The e.m.f. of the thermocouple was measured with a Leeds and Northrup Model 8662 potentiometer. The bath was warmed up slowly and a series of temperature *vs.* height-of-liquid readings were made between −8 and +25°. The volume of the pentaborane was calculated to the nearest 0.001 ml.

Results and Discussion

The scale on the densitometer was read to the nearest 0.25 mm. which corresponds to an uncertainty in the density of ±0.05%. The measurement of temperature was accurate to ±0.3° which corresponds to an uncertainty in density of ±0.05%. The maximum weighing error was less than 0.1%. The net variability, therefore, should be no larger than 0.3%. This leads to a value of 0.637 ± 0.002 g./ml. for the density of pentaborane at 0°.

This value is essentially in agreement with that of Smith and Miller[2] and indicates that the value of Stock[1] is in error.

[5] Ohio State University Research Foundation, Technical Report No. 6 (Project RF-309), "The Heat Capacity of Pentaborane from 13° to 296°K.," 1949.

REACTION MOTORS, INC.
DENVILLE, N. J.

The Crystal Structure of Rhenium Monosilicide

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Recently we investigated the phases formed by reaction of silicon with rhenium.[3] The crystal structure of one of the phases, whose composition was shown by a comparison of X-ray diffraction powder patterns with compositions to be $ReSi_{1.0\pm0.1}$, has been determined from X-ray powder data.

Experimental

Preparative procedures have been described previously.[3] Diffraction data were obtained for the structure determination from five hour exposures with copper $K\alpha$ radiation. Density of the ReSi phase was measured by water displacement of a powder sample.

Results and Discussion

All lines of diffraction patterns from heated equimolar mixtures could either be fitted to a cubic unit cell with $a = 4.775 \pm 0.002$ Å. (Cu $K\alpha_1 = 1.54050$ Å. and Cu $K\alpha_2 = 1.54434$ Å.) or could be identified as lines of another rhenium–silicon phase. The unit cell has a calculated density of 13.1 g. cm.$^{-3}$ if it is assumed to contain four molecules of ReSi. The experimental density is 13.4 ± 0.6 g. cm.$^{-3}$.

Previous workers have shown that FeSi,[4,5] CoSi,[4] MnSi[4] and RhSi[6] all belong to space group T^4-$P2_13$ with metal and silicon atoms in two sets of fourfold (a) positions: x,x,x; $^1/_2 + x, {}^1/_2 - x, -x$; $^1/_2 - x, -x, {}^1/_2 + x$; $-x, {}^1/_2 + x, {}^1/_2 - x$. In all those silicides the values of x were about 0.84 for the silicon atoms and 0.14 for the metal atoms.

The planes found for ReSi were those to be expected if it is isostructural with FeSi. Intensities of diffraction lines accordingly were calculated on the assumption that ReSi has the FeSi structure with $x = 0.84$ for the silicon atoms and $x = 0.14$ for the rhenium atoms. The equation $I = 10^{-5}\cdot F^2P(1 + \cos^2 2\theta)/\sin^2\theta \cos\theta$, in which all terms have their usual meaning, was used for intensity calculations. Plane assignments, observed and calculated planar spacings, and observed and calculated intensities are presented in Table I.

TABLE I

DIFFRACTION DATA FOR ReSi

Plane	Spacing (Å.) Obsd.	Calcd.	Intensity Obsd.[a]	Calcd.
110	3.375	3.376	M+	52
111	2.749	2.757	M	24
200	2.391	2.388	VW	3.7
210	2.132	2.135	VS	90
211	1.949	1.949	S	38
220	1.686	1.688	VVW	0.2
221	1.593	1.592	VVW	3.0
310	1.509	1.510	M	14.7
311	1.438	1.440	M	11.5
222	1.376	1.378	M	9.8
320	1.322	1.324	M	13.5
321	1.275	1.276	M+	15.4
400	1.192	1.194	M	6.8
322, 410	1.158	1.158	VVW	2.7
330, 411	1.125	1.125	W	6.8
331	1.095	1.095	W	7.4
421	1.041	1.042	M+	16.7
332	1.018	1.018	W	3.5
422[b]	0.9728	0.9747	VVW	1.2
431, 510	.9361	.9365	M	12.3
333, 511	.9187	.9189	M	8.3
432, 520	.8867	.8867	S	26
521	.8718	.8718	M	9.9
440	.8442	.8441	M	9.8
433, 530	.8190	.8190	M	12.2
531	.8071	.8071	M	8.8
610	.7850	.7850	M+	18.3
611, 532	.7745	.7746	VS	105

[a] S = strong, M = moderate, W = weak, V = very.
[b] The last ten spacings are for Cu $K\alpha_1$ reflections.

Agreement between observed and calculated planar spacings and agreement between observed and calculated intensities are good. The precision of the visually estimated intensity data does not warrant attempts to fix the values of x for rhenium and silicon more closely, however.

It can be concluded that ReSi belongs to space group T^4-$P2_13$ with $x \sim 0.84$ for silicon atoms and $x \sim 0.14$ for rhenium atoms. No indication of variability in composition of the phase was found.

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[3] A. W. Searcy and R. A. McNees, Jr., THIS JOURNAL, **75**, 1578 (1953).

[4] B. Boren, *Ark. Kemi Min. Geol.*, **11A**, 1 (1933).

[5] L. Pauling and A. M. Soldate, *Acta Cryst.*, **1**, 212 (1948).

[6] S. Geller and E. A. Wood, *ibid.*, **7**, 441 (1954).

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Stability of the Histamine Chelates[1]

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The structural requirements for histaminic activity have been summarized by Hofmann.[2] The majority of active compounds are those capable of forming a six-membered ring between a 2-amino side chain nitrogen, a tertiary nitrogen of an aromatic nucleus, and some polar center. Niemann and Hays[3] suggested that one characteristic of the histamine-active molecule was its ability to undergo hydrogen bonding between basic nitrogen atoms. A related consideration is that of metal chelate formation. The histamine-active structure also is capable of forming a six-membered ring about a metal ion such as that of a metal–protein or metal activated enzyme.

In order to act as a mediator of binding between small molecules and proteins, a metal ion must be capable of forming an independent complex with the small molecule.[4] Preliminary to mediation binding studies, the nature and stabilities of the Cu^{II}, Ni^{II} and Co^{II} chelates of histamine, 4(5)-(2-aminoethyl)-imidazole, were investigated. The consecutive formation constants for these chelates, at 25°, were reported previously.[5] A maximum of three histamine molecules was indicated to be bound by nickel and cobaltous ions in contrast to copper which added two histamine ligands. The separate contributions to chelate stability of the imidazole and amino nitrogen atoms are reported in this paper. The structures and stabilities of the chelates have been considered in terms of the successive formation constants and the thermodynamics of complex formation.

Experimental

The potentiometric technique of Bjerrum[6] was used. Final values of the formation constants were obtained by successive approximation. In solving for the constants of imidazole, temporary constants were chosen which were small for k_N; this is necessary since the approximation equations for the first and last constants are limiting expressions, only.

Imidazole was obtained from the Eastman Kodak Co., Rochester, N. Y., and was purified by recrystallization from benzene. Recrystallization yielded a product of m.p. 89.0–89.5° (lit. 90°). Nitrogen analysis indicated a purity of 98.4%. Approximately 3 M solutions were made up in 0.1 N KCl and were standardized potentiometrically.

Results

Logarithmic values of the successive formation constants, k_n, are listed in Table I. All constants were determined at ionic strength 0.135.

TABLE I

SUCCESSIVE CONSTANTS FOR THE REACTIONS OF HISTAMINE AND RELATED COMPOUNDS WITH VARIOUS CATIONS, 0 AND 25°

Base	Cation	log k_n			
	n =	1	2	3	4
Ethylamine	H^+	10.8[a]			
		11.4			
Imidazole	H^+	7.09			
		7.63			
	Cu^{II}[b]	4.20	3.47	2.84	2.0
		4.72	3.90	3.28	2.3
	Ni^{II}[c]	2.94	2.41	1.99	1.3
		3.36	2.79	2.24	1.3
Histamine[d]	H^+	9.88	6.13		
		10.5	6.63		
	Cu^{II}	9.55	6.48		
		10.1	6.90		
	Ni^{II}	6.88	5.03	3.09	
		7.24	5.25	3.26	
	Co^{II}	5.27	3.68	2.03	
		5.37	3.81	2.07	

[a] Upper values at 25°, lower values at 0°. [b] These values compare to 4.36, 3.57, 2.85 and 2.05 at 22.5° as converted from the intrinsic constants of J. T. Edsall, G. Felsenfeld, D. S. Goodman and F. R. N. Gurd, THIS JOURNAL, **76**, 3054 (1954). [c] It is not possible to determine whether n_{max} = 4 or 6 for nickel–imidazole by means of the Bjerrum technique. Recent polarographic data of N. C. Li, T. L. Chu, C. T. Fujii and J. M. White, *ibid.*, **77**, 859 (1955), indicate that the hexacovalent complex is formed. Values of 3.27, 2.68, 2.15 and 1.65 were published for the first four constants at 25°. [d] A. Albert, *Biochem. J.*, **50**, 693 (1952), has cited log k_1k_2 values for the copper, nickel and cobaltous chelates of 16.2, 11,7 and 8.7, respectively. Values of about 8.6 were calculated for the histamine–Co^{II} system by J. Z. Hearon, D. Burk and A. L. Schade, *J. Natl. Cancer Inst.*, **9**, 337 (1949). No constants were listed for uptake of the third histamine ligand by hexacovalent ions.

Enthalpy and entropy changes for the ionization of ethylamine, imidazole and the corresponding groups of histamine are similar. The heat of formation of primary aminium ion is −9 kcal. mole^{-1} in both histamine and ethylamine; the corresponding entropy changes are approximately 15 and 19 e.u. Heats and entropies for the protonation of imidazole nitrogen are −8 to −7 kcal., and about 4 e.u. in the mono- and diacidic bases.

The probable structures of the histamine chelates may be described in terms of the successive formation constants. The difference between these consecutive constants is much larger for bis-histamine–Cu(II) ion than in the corresponding chelates of nickel and cobalt. This indicates the expected steric opposition to formation of the square planar copper bonding configuration. In bis-trimethylenediamine–Cu(II), the difference between log k_1 and log k_2 is 2.60.[7] If log k_2 for the trimethylenedia-

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(1) Portion of a dissertation presented by B. L. Mickel as partial fulfillment of the requirement for the degree Doctor of Philosophy in chemistry at Kansas State College, 1955. This investigation was supported by a research grant G 3920 from the National Institutes of Health, Public Health Service.

(2) Klaus Hofmann, "Imidazole and its Derivatives," Interscience Publishers, New York, N. Y., 1953.

(3) C. Niemann and J. T. Hays, THIS JOURNAL, **64**, 2288 (1942).

(4) Irving M. Klotz and W. C. Loh Ming, *ibid.*, **76**, 805 (1954).

(5) B. L. Mickel and A. C. Andrews, *ibid.*, **77**, 323 (1955).

(6) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941, pp. 198–219.

(7) H. Irving, R. J. P. Williams, D. J. Ferrett and A. E. Williams, *J. Chem. Soc.*, 3494 (1954).