Fig. 2 might still be attributable to weak nickel phosphate complexes undetected by the preliminary experiments. Unfortunately, the lack of analytical sensitivity in the preliminary systems made complete duplication of phosphate to nickel ratios impossible.

TABLE II

PRECISION BASED ON THE CALCULATED VALUE OF DISSOCIATION CONSTANT FOR EACH EQUILIBRATION SOLUTION

Ionic strength	Mean value $K_D \times 10^{31}$	Absolute stand dev.	No. of equilibration soln.
0.100	0.5	±0.11	15
.048	0.7	± .18	14
.014	1.0	± .28	14
.0028	0.9	± .20	14

Mean value K_D extrapolated to infinite dilution is $1.0 \pm 0.2 \times 10^{-31}$.

The dissociation constants obtained from the intercepts of Fig. 2 are extrapolated to infinite dilution in Fig. 3, yielding a dissociation constant for the tetracyanonickelate(II) species of 1×10^{-31}.

A summary of the experimental values for the cumulative dissociation constant of tetracyanonickelate(II) is given in Table II.

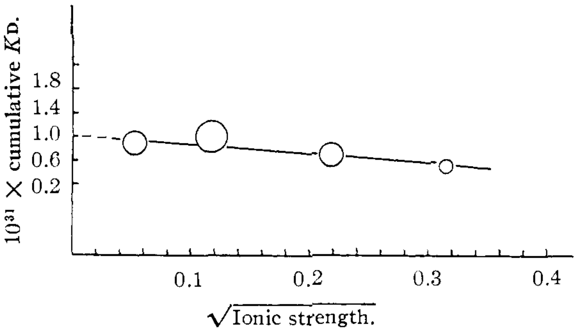

Fig. 3.—Plot of cumulative dissociation constant of tetracyanonickelate(II) *vs.* square root of ionic strength.

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CORVALLIS, OREGON

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF CONNECTICUT]

Cation Substitution in Perovskite-like Phases[1,2]

BY E. J. FRESIA, LEWIS KATZ AND ROLAND WARD

RECEIVED MARCH 23, 1959

Several phases with a face-centered cubic structure representing an ordered perovskite-like arrangement of cations have been prepared having the general formula $A(B_{0.5}{}^{II}W_{0.5}{}^{VI})O_3$ where A = Ba or Sr and B^{II} = Zn, Fe, Co, Ni. The strontium compounds show a tetragonal distortion at room temperatures but become cubic at elevated temperatures. Phases of the type $Sr_xBa_{(1-x)}(Zn_{0.5}W_{0.5})O_3$ are cubic at room temperatures over the range $0 < x < 0.4$. $Sr_{0.5}Ba_{0.5}(Zn_{0.5}W_{0.5})O_3$ becomes cubic above 300° whereas $Sr(Zn_{0.5}W_{0.5})O_3$ becomes cubic at 570°. The cubic structure appears when the Goldschmidt tolerance factor, calculated from the weighted averages of the A and B cations, is 0.89 or greater.

Introduction

Compounds with the type formula A_3WO_6 (where A = an alkaline earth cation) have been shown by Steward and Rooksby[3] to have structures related to that of perovskite and may be written $A(A_{0.5}W_{0.5})O_3$ to indicate that half of the octahedral B-cation sites are occupied by A cations. Moreover the cations in the B-sites are ordered in such a manner that the unit cell edge must be doubled giving a large face-centered cubic structure with lattice constant about 8 Å. A similar structure and ordering of the cations in B-sites has been observed in $A(La_{0.5}Ta_{0.5})O_3$[4] and in the oxygen-deficient phases $A(A_{0.5}Ta_{0.5})O_{2.75}$[4] and $A(A_{0.5}Nb_{0.5})O_{2.75}$.[5] It is not surprising, therefore, to find that other ions may be introduced into the B-positions to yield similar structures. This paper is concerned with the compounds $A(B_{0.5}{}^{II}W_{0.5})O_3$ where A = Sr or Ba and B^{II} = Zn, Fe, Co, Ni.

Experimental

Reagents.—Barium oxide was prepared from the peroxide at 950° *in vacuo*, strontium oxide by heating the carbonate in hydrogen at 1150° for 48 hr., cobaltous oxide by heating the carbonate in an argon atmosphere. Iron(II) was introduced by using equimolar proportions of metallic iron and Fe_2O_3. The other reactants were C.P. or reagent grade chemicals. X-Ray diffraction data were obtained using a Philips X-ray camera of radius 57.3 mm. Ten hour exposures were made using copper K_α radiation. A Central Research Laboratories high temperature camera model H(10), radius 57.3 mm., was used for following crystallographic transformations.

Intimate mixtures of the reactants in proportion to give $A(M_{1/2}W_{1/2})O_3$ (A = Sr, Ba; M = Fe, Co, Ni, Zn) were heated for 24 hr. at 1100 to 1250°. The nickel and zinc compounds were prepared by heating in air using zirconium silicate boats as containers, whereas the iron and cobalt compounds were made in evacuated silica capsules. The mixtures were reground several times during the heating period. Some preparations were obtained by first preparing zinc tungstate and then heating this compound with the alkaline earth oxide. In all cases small amounts of the alkaline earth tungstate could be detected in the final product. No procedure was found to prevent its formation or to remove it from the principal phase. It seemed clear from X-ray data,

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[1] Taken in part from the Masters Thesis submitted by E. J. Fresia to The University of Connecticut, 1958.

[2] Part of this work was supported by the Office of Naval Research. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[3] E. G. Steward and H. P. Rooksby, *Acta Cryst.*, **4**, 503 (1951).

[4] L. H. Brixner, THIS JOURNAL, **80**, 3214 (1958).

[5] F. Galasso, L. Katz and R. Ward, *ibid.*, **81**, 820 (1959).

however, that the main products of the reaction were phases of composition $A(M_{1/2}W_{1/2})O_3$. In Table I a comparison is given of the observed interplanar spacings and intensities of reflections and those calculated on the basis of the compound $Ba(Zn_{1/2}W_{1/2})O_3$ having an ordered cubic perovskite configuration with lattice constant 8.116 Å. None of the phases in which A is solely strontium was found to be cubic at room temperatures, but all of those investigated could be indexed on the assumption of a slight tetragonal distortion of the large perovskite cube with $c/a > 1$. Table II gives the indexing of the compound $Sr(Ni_{1/2}W_{1/2})O_3$.

TABLE I

$Ba(Zn_{1/2}W_{1/2})O_3$

hkl	d_{obsd}	d_{calcd}	$I_{(obsd)}$	$I_{(calcd)}$
111	4.701	4.683	m	2.5
220	2.873	2.869	s^{++}	100
311	2.453	2.448	m^-	1.6
222	2.345	2.343	w	0.52
400	2.033	2.029	s	33
331	1.860	1.862	w^+	0.69
422	1.657	1.656	s^+	34
511, 333	1.562	1.562	w^-	0.51
440	1.433	1.434	s^-	17
531	1.371	1.372	w^-	0.48
620	1.284	1.283	s^-	17
533	1.236	1.237	$w^=$	0.17
622	1.223	1.223	$w^\equiv$	0.05
444	1.171	1.171	m^+	5.0
711, 551	1.137	1.136	w^-	0.25
731, 553	1.056	1.056	w^-	0.32

TABLE II

$Sr(Ni_{1/2}W_{1/2})O_3$

FORWARD REFLECTIONS—TETRAGONAL INDEXING

I_{obsd}	d_{obsd}	d_{calcd}	*hkl*
m^+(B)	4.54	4.55	111
m(B)	3.95	3.96	002
		3.94	200
w	3.21	3.22	112
		3.21	211
s^{++}(B)	2.79	2.79	202
		2.78	220
$w^{\equiv a}$	2.70		
m^+(B)	2.38	2.38	113
		2.37	311
$w^=$	2.273	2.275	222
$w^{=a}$	2.002		
m	1.978	1.979	004
s	1.962	1.966	400
w(B)	1.806	1.810	313
		1.804	331
w^-(B)	1.760	1.768	204
		1.761	402
		1.758	420
$w^{=a}$	1.645		
s^+(B)	1.605	1.612	224
		1.606	422
w	1.513	1.516	333
s(B)	1.392	1.394	404
		1.390	440

[a] Lines belonging to pattern of $SrWO_4$.

The lattice constants of all the compounds are listed in Table III. Solid solutions of the type $Ba(M_x'M_{(0.5-x)}W_{0.5})O_3$ were examined where M = Zn and M′ = Ni or Co and where M = Ni and M′ = Co. A linear relationship between lattice constant and x was found in each case.

TABLE III

LATTICE CONSTANTS OF $A(M_{1/2}W_{1/2})O_3$ COMPOUNDS

Compound	Cell edge, Å.
$Ba(Ca_{1/2}W_{1/2})O_3$	8.390[3]
$Ba(Zn_{1/2}W_{1/2})O_3$	8.116
$Ba(Fe_{1/2}W_{1/2})O_3$	8.133
$Ba(Co_{1/2}W_{1/2})O_3$	8.098
$Ba(Mg_{1/2}W_{1/2})O_3$	8.099[3]
$Ba(Ni_{1/2}W_{1/2})O_3$	8.066
$Sr(Zn_{1/2}W_{1/2})O_3$	a = 7.92
	c = 8.01
$Sr(Co_{1/2}W_{1/2})O_3$	a = 7.89
	c = 7.98
$Sr(Ni_{1/2}W_{1/2})O_3$	a = 7.86
	c = 7.91

It was of some interest to consider the substitution of strontium for barium in these compounds since the barium compounds all appear to be cubic and the strontium compounds appear to be tetragonal. (It should be pointed out that the crystal systems are inferred from the fact that the X-ray powder patterns can be indexed reasonably well; the systems have not otherwise been confirmed. For simplicity, the compounds will be referred to as cubic or tetragonal even though the systems cannot be considered as fully established.) A series of phases of composition $Sr_xBa_{1-x}(Zn_{1/2}W_{1/2})O_3$ was found to be cubic over the range $0 \leq x < 0.4$. The distortion from the cubic lattice manifests itself by the splitting of the lines in the back-reflection region. The splitting becomes more pronounced with increasing proportions of strontium between x = 0.4 and 1.0. It is assumed that the distortion of the intermediate phases is also tetragonal. Because higher symmetry is obtained by the substitution of the larger A cation, it was to be expected that rising temperature would bring about a similar change, especially since Steward and Rooksby found that this occurred with one of the distorted alkaline earth tungstates.

X-Ray powder diagrams were taken with the high temperature camera at various temperature intervals up to 900°. The samples were held in silica capillaries. In this way it was found that $Sr(Ni_{1/2}W_{1/2})O_3$ became cubic at about 400°, $Sr(Zn_{1/2}W_{1/2})O_3$ at about 570° and the phase $Sr_{1/2}Ba_{1/2}(Zn_{1/2}W_{1/2})O_3$ near 300°.

Magnetic susceptibilities of two nickel compounds were determined at room temperatures. The cubic $Ba(Ni_{1/2}W_{1/2})O_3$ gave μ_B = 2.78 Bohr magnetons while the tetragonal $Sr(Ni_{1/2}W_{1/2})O_3$ gave a slightly higher value of 2.96 Bohr magnetons.

Attempts were made to prepare compounds of the type $Ba(M_{2/3}W_{1/3})O_3$ where M is a trivalent element. Analogous compounds such as $Ba(Zn_{1/3}Ta_{2/3})O_3$ have been shown to have a structure related to the perovskite.[5] The trivalent elements used were scandium and indium. The sesquioxides were mixed with appropriate proportions of tungsten(VI) oxide and barium oxide. The mixture containing indium oxide, which is somewhat volatile, was heated at 750°, but the preparation of the scandium compound was carried out at 1100°. The diffraction patterns of the products bore a strong resemblance to those of the phases containing a divalent cation in the B-position. The X-ray powder pattern for the scandium compound was indexed on the basis of a face centered cubic cell with a = 8.24 Å. Two possible formulas compatible with a face centered cubic structure are $Ba_{3/4}(Sc_{1/2}W_{1/2})O_3$ and $Ba[Sc_{1/2}(Sc_{1/6}W_{1/3})]O_3$. Upon heating appropriate quantities of the oxides for the stoichiometry of the first of these compounds, a product containing much more barium tungstate and less of the face-centered cubic phase was obtained. The barium deficient formula, therefore, is not very likely. These systems were not investigated further.

Discussion

Among the compounds listed in Table III are the calcium and magnesium compounds which were studied by Steward and Rooksby[3] who state that the magnesium compound is slightly distorted from the cubic structure. We found no evidence to suggest that the nickel compound was distorted, perhaps because of the limits of resolution of our cameras. The Goldschmidt tolerance factor $t = (R_A + R_0)/\sqrt{2}(R_B + R_0)$, however, is 0.94 for the nickel and the magnesium compounds (using the observed ionic radii listed by Wyckoff.[6] On this ground the expected structure would be cubic. It is interesting to note that for the $Sr_xBa_{1-x}(Zn_{1/2}W_{1/2})O_3$ phase, using a weighted average of Sr^{+2} and Ba^{+2} radii for the A cation radius, the tolerance factor falls to 0.89 at $x = 0.4$. This represents the highest concentration of strontium for which a cubic structure was found experimentally.

Since the cubic structure can be described in terms of closest packing of oxide ions and A cations, it seems reasonable to attribute the tetragonal distortions to the unfavorable packing of the small strontium ions. The slight difference in magnetic susceptibility of the cubic and tetragonal nickel compounds indicates no difference in bonding in the two crystals. This conclusion is compatible with the supposition that the symmetry is determined by ionic packing.

STORRS, CONN.

[6] R. W. G. Wyckoff, "Crystal Structures," Interscience Publishers, New York, N. Y., 1948, Section I.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, DREXEL INSTITUTE OF TECHNOLOGY]

Cyclohexylhalosilanes. Reaction of Cyclohexylsilane with Silver Isocyanate and Isothiocyanate[1]

BY HERBERT H. ANDERSON

RECEIVED MARCH 25, 1959

This paper establishes the direct, partial replacement of hydrogen by halogenoid in certain alkylsilanes, with yields of 41–44%. In a new modification, gradual addition of AgX to excess cyclo-$C_6H_{11}SiH_3$ furnishes cyclo-$C_6H_{11}SiH_2X$ and some cyclo-$C_6H_{11}SiX_3$; X is the halogenoid NCO or NCS. Oxidation of excess cyclo-$C_6H_{11}SiH_3$ with $HgSO_4$ or HNO_3 furnishes polymeric (cyclo-$C_6H_{11}SiO)_2O$ rather than (cyclo-$C_6H_{11}SiH_2)_2O$. Three reactions of (cyclo-$C_6H_{11}SiH_2)_2O$ follow: with warm, concentrated hydrofluoric acid to give impure cyclo-$C_6H_{11}SiH_2F$ and some hydrogen; with hot gaseous HCl and P_4O_{10} to give a 25% yield of pure cyclo-$C_6H_{11}SiH_2Cl$; with a deficiency of warm iodine to give gaseous HI, cyclo-$C_6H_{11}SiH_2I$ and a viscous liquid probably (cyclo-$C_6H_{11}SiHO)_3$ or $_4$. Shaking cyclo-$C_6H_{11}SiCl_3$ with excess aqueous hydrofluoric acid furnishes cyclo-$C_6H_{11}SiF_3$ easily. Table I lists the properties of 11 new compounds containing the cyclo-C_6H_{11}-Si linkage.

Introduction

Four earlier papers establish the use of halides of certain transitional elements and elements in regular groups for the replacement of hydrogen attached to tin[2a] in $(C_2H_5)_3SnH$, to germanium[2b] in $(C_2H_5)_3GeH$ or to silicon first[3] in $(C_2H_5)_3SiH$ and later[4] in n-$C_7H_{15}SiH_3$. Gradual addition of $HgCl_2$ or $HgBr_2$ to an excess of $(C_2H_5)_2SiH_2$ or n-$C_7H_{15}SiH_3$ allows straightforward preparation of $(C_2H_5)_2SiHCl$, $(C_2H_5)_2SiHBr$, n-$C_7H_{15}SiH_2Cl$ and n-$C_7H_{15}SiH_2Br$, respectively[3,4]; this is apparently a new modification for the preparation of organosilicon compounds containing both Si–H and Si–Cl or Si–Br. In these papers the two main explanations for the reaction of $(C_2H_5)_3SnH$, $(C_2H_5)_3GeH$ or $(C_2H_5)_3SiH$ with a given halide depend on heats of formation per equivalent of available halogen in the compounds and on the appropriate ionization potentials of the elements.

This paper, in turn, reports the reaction of cyclo-$C_6H_{11}SiH_3$ with AgNCO or AgNCS to give moderate yields of cyclo-$C_6H_{11}SiH_2NCO$ or cyclo-$C_6H_{11}SiH_2NCS$, respectively, together with some cyclo-$C_6H_{11}Si(NCO)_3$ or cyclo-$C_6H_{11}Si(NCS)_3$; this is apparently a new modification. This paper also studies the separate reactions of (cyclo-$C_6H_{11}SiH_2)_2O$ with aqueous HF, anhydrous HCl and iodine. Table I lists the properties of 11 new compounds—and also cyclohexylbromosilane, previously mentioned without data.[5]

Experimental Results

Table I lists the conditions of distillation, the boiling points, densities, refractive indices, molar refractions and the analyses of 11 new compounds and cyclohexylbromosilane. There is one complete series: $RSiH_3$, $RSiH_2I$, $RSiHI_2$ and $RSiI_3$. Table I lists cyclo-$C_6H_{11}SiH_2NCO$ and cyclo-$C_6H_{11}SiH_2NCS$, both prepared from cyclo-$C_6H_{11}SiH_3$ and AgNCO or AgNCS, respectively. Shaking cyclo-$C_6H_{11}SiCl_3$ with excess aqueous hydrofluoric acid yields cyclo-$C_6H_{11}SiF_3$ easily.

Experimental

Equipment for all reactions employed ground joints throughout. There were also micro-pycnometers, micropipets for the measurement of liquids and the subsequent titration of available acidity, transfer pipets and special equipment for determining H present as Si–H.

Cyclohexylsilane.—Although cyclohexylsilane is available in 38% yield through reaction[6] of cyclo-$C_6H_{11}MgCl$ with SiH_3Br, the preparation was via $LiAlH_4$[7] and commercial cyclo-$C_6H_{11}SiCl_3$. After dissolving 21 g. of $LiAlH_4$[7] in 300 ml. of diethyl ether, there followed addition of 122 g. of cyclo-

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[1] Presented at 136th National Meeting of the A. C. S., Atlantic City, N. J., September, 1959.

[2] (a) H. H. Anderson, THIS JOURNAL, **79**, 4913 (1957); (b) **79**, 326 (1957).

[3] H. H. Anderson, *ibid.*, **80**, 5083 (1958).

[4] H. H. Anderson and A. Hendifar, *ibid.*, **81**, 1027 (1959).

[5] W. S. Miller and others, *ibid.*, **79**, 5605 (1957).

[6] H. E. Opitz and others, *ibid.*, **78**, 293 (1956).

[7] A. E. Finholt and others, *ibid.*, **69**, 2692 (1947).