AsF_3 in acetonitrile, or to pure AsF_3. The observed increased shielding of the fluorine nucleus is to be expected if complexing occurred. However, a small shift to higher field would also occur if the rate of exchange in the mixture was increased to the extent that the three bands coalesced.

In an equimolar mixture of AsF_3 and $AsCl_3$ containing an equivalent amount of base, the disappearance of the two small bands B and C could be due to complex formation. Even if the base is present in slightly less than an equivalent amount, reduction in the amount of one of the free symmetrical trihalides through complex formation could have occurred to such an extent that the concentration of the exchanged species was below the level of detection. However, in a mixture containing $AsCl_3$, AsF_3, and pyridine in a 10:10:1 mole ratio, substantial amounts of the free trihalides will still be present even if complex formation does occur.[13] Therefore observable amounts of the exchanged products would be expected in this mixture. Since the small bands (B and C) were not observed, it is concluded that, at least in this case, the addition of pyridine resulted in an increase in the rate of exchange.

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(13) The implicit assumption made is that a complex of the constitution pyridine·$10AsX_3$ is not stable in the mixture. Exchanged species would be detected even if the complex pyridine·$9AsF_3$ was inert.

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The Hydrothermal Synthesis of Sodium Amphiboles

BY T. E. GIER, N. L. COX, AND H. S. YOUNG

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Sodium magnesium silicates with the amphibole structure have been obtained as fine, exceptionally flexible fibers up to 4 in. long from a Na^{+}–Mg^{+2}–SiO_3^{-2} system under hydrothermal conditions. Co^{+2} and Ni^{+2} substitute entirely or partially for magnesium in the structure to give pink and green fibers, respectively.

Introduction

The term amphibole describes a large class of naturally occurring metal silicates whose distinctive feature is a double chain of (SiO_4) tetrahedra as the fundamental element of the crystal structure. A number of X-ray structure determinations of amphiboles have been made,[1–5] and the silicate chains have been shown to be held together face to face in the crystal by octahedrally coordinated cations and edge to edge by cations in hexahedral (pseudo-cubic) coordination. The crystal structure of the amphiboles is susceptible in nature to extensive substitution at different sites by a variety of cations present in the original magma or during subsequent metamorphism. As a result, probably over 100 amphiboles have been described, each differing slightly in stoichiometry. The mineralogical literature contains many references to the composition[6–8] and synthesis[9–14] of representative members of this class of silicates. This paper is concerned with (1) the hydrothermal synthesis of sodium magnesium amphiboles and fluoro amphiboles as fine, extremely flexible fibers from simple aqueous systems containing Na^{+}, Mg^{+2}, SiO_3^{-2} (or polymers thereof), and F^{-}; and (2) fine, fibrous sodio-amphiboles in which the magnesium is replaced partially or entirely by Co^{+2} or Ni^{+2}.

Experimental

Materials.—Reactants were analytical reagent grade chemicals from conventional sources. Colloidal SiO_2 was base-stabilized "Ludox"[15] LS (15% SiO_2) or SM (30% SiO_2). All solutions were prepared with distilled water.

Apparatus and Procedures. Syntheses.—The syntheses were carried out in collapsible capsules fabricated from 0.375–1.0 in. diameter platinum tubing having a wall thickness of 0.005 in. with crimped and welded end closures. The capsules were charged with the reagent solutions (usually 1–2 *M*) in the desired ratios, leaving 30–50% of the capsule volume empty prior to final sealing. This free volume prevented rupture of the capsules during heating. The capsules were then placed in a heavy-walled pressure vessel, pressured to about 1000 atm. with argon

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(15) Industrial and Biochemicals Dept., E. I. du Pont de Nemours and Company.

or water, and heated to the synthesis temperature of 575–700°, with pressure maintained from 2000 to 3000 atm. for 6 hr. The pressure vessel was then cooled to 150–200° (7–8 hr.), the pressure released (to expand the capsules to facilitate product removal), and the vessel unloaded after rapid cooling to room temperature with an air blast. The recovered capsules were then opened, and the product was washed thoroughly (to neutrality) and dried in a vacuum oven at 110° for at least 8 hr. or longer if the fiber masses were dense.

Analyses.—Sodium was determined by flame photometry by comparison with carefully prepared standards. In the absence of fluoride ion, silicon was determined by a standard alkaline fusion, ashing, solution in HCl, and weight loss of the ultimate residues after treatment with $HF-H_2SO_4$. If fluoride ion was present, it was removed by complexing as BF_4^- prior to operation on the residues.[16] Magnesium, cobalt, and nickel were determined by removing the silica ($HF-H_2SO_4$) and titrating the resulting solution with ethylenediaminetetraacetic acid. Weight losses were determined by bringing the sample to constant weight at 1000°.

X-Ray diffraction patterns were obtained with Cu Kα or Co Kα radiation. A Debye-Scherer powder camera was used to record the patterns. Fiber repeat distances were determined by means of a rotation camera.[17]

Results and Discussion

X-Ray studies in recent years[1,4,6] have defined the basic amphibole structure. The stoichiometry of the structure is most conveniently generalized as $WX_2Y_5(Si_4O_{11})_2(OH,F)_2$,[18] where W represents a cation coordinated in a "back" channel and appears to be only rarely occupied, X represents cations coordinated (8-fold) at the edge of the chains, Y represents cations coordinated octahedrally at the faces of the chains, and each Si is tetrahedrally coordinated to oxygen in the double chain. Schematic diagrams of the arrangement of the SiO_4 chains in the amphibole structure are available in the literature.[8,19,20] On this basis an average of seven or eight (maximum) *metal* ions may be present for each $(Si_4O_{11})_2(OH,F)_2$ unit of the chain and these must supply a positive charge of +14 units for electrical neutrality of the crystal. If the cations do not conform to this requirement, protons must enter the structure to permit balance. Presumably this occurs as OH^- units which retain the same coordination as the O^{-2} unit which is replaced; at the present time, the exact location of these additional protons cannot be designated with certainty.

Hydrothermal Syntheses of Fibrous Sodium Magnesium Amphiboles.—Sodium magnesium amphiboles have been synthesized with a range of stoichiometries using hydrothermal techniques. Solutions of 1 *M* $MgCl_2$, 2 *M* Na_2SiO_3, colloidal silica, and (if desired) 1 *M* NaF were charged in selected proportions to the collapsible platinum tubes, and the resulting gel was crystallized at elevated temperature and pressure as densely intertangled fibers with diameters of 0.1–3 μ and lengths up to 4 in. The nature of the products was sensitive to time, pressure, and temperature as well as charge composition. (In this paper, we designate charge compositions as a ratio of four numbers, representing, in order (a) unit mole proportion of Mg^{+2}, Co^{+2}, or Ni^{+2} expressed as hydroxide, (b) moles of Si as SiO_2, (c) moles of residual NaOH (*e.g.*, after reaction of the basic Na_2SiO_3 with divalent metal chloride), and (d) moles of NaF. For example, if a charge is prepared from 10 ml. of 1 *M* $MgCl_2$, 10 ml. of 2 *M* Na_2SiO_3, 5.0 ml. of 2 *N* NaOH, and 2.52 g. of NaF (60 moles) with added water to fill the capsule to the desired volume, the charge composition specification is 1:2:3:6.) At the more severe conditions (700°, 3000 atm.) and with a relatively large excess of free NaOH in the charge, only nonacicular forsterite (Mg_2SiO_4) is recovered. If the basicity of the menstruum is decreased, however, essentially quantitative yields (based on Mg^{+2} charged) of the fibrous sodium magnesium amphibole are produced. The relationships between the product stoichiometry and the composition of the charge are shown in Table I. The addition of F^- to the charge results in a fluoride-containing, fibrous amphibole (1:2:3:6 charge ratio).

Synthesis of Other End-Members of the Sodium Amphibole Series.—Magnesium (r = 0.66 Å.; Ahrens) is only one of several divalent cations which can satisfy requirements of ion size and charge density for incorporation at the Y position in the amphibole structure. For example, replacement of $MgCl_2$ by $CoCl_2$ (r = 0.72 Å.) or by $NiCl_2$ (r = 0.69 Å.) resulted in reproducible recovery of high yields of the corresponding sodium cobalt and sodium nickel amphiboles in fibrous form.

The sodium cobalt amphibole structure is easily prepared, although the optimum conditions are somewhat different from those for the sodium magnesium amphibole. Too high basicity results in contamination of the pink fibers with black Co_3O_4 at the high temperature end of the synthesis range, and coarsening of the fibers to needles becomes noticeable. A 1:3:2:0 charge run at 575° (2000 atm.) for 6 hr. resulted in fine fibers of the amphibole structure.

The sodium–nickel silicate system yields fine, flexible, pale green fibers with the amphibole structure, but in this case prolonged treatment at relatively high basicity and temperature is necessary to minimize the formation of other unidentified phases. For example, a charge ratio of 1:6:4:0 held at 700° (3000 atm.) for 6 hr. gives the fibrous amphibole with only small amounts of unidentified material. Partial replacement of magnesium by cobalt or nickel is also possible to give mixed sodium amphibole structures. In one experiment, an amphibole containing magnesium and iron was prepared, but no effort was made to identify the location of the iron species (examples 4 and 5, Table I).

X-Ray Studies.—All products from the hydrothermal synthesis studies were analyzed by X-ray powder pattern techniques. Additional information was ob-

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TABLE I

AMPHIBOLES

Example no.	Charge ratio[a]	Syn. conditions	Product stoichiometry[b]	Comments
1	1(Mg):6:10:0	700°, 3000 atm., 6 hr.	$Na_{2.5}H_{1.5}(Mg_5)Si_8O_{22}(OH)_2$	Fine, long fibers. Entrance of Mg^{+2} into X position not likely
2	1(Mg):2:2:0	700°, 3000 atm., 6 hr.	$Na_{2.2}H_{0.6}Mg_{0.6}(Mg_5)Si_8O_{22}(OH)_2$	Fine, long fibers. Partial entrance of Mg^{+2} into X position
3	1(Co):3:2:0	575°, 2000 atm., 6 hr.	$Na_{2.44}H_{0.75}Co_{0.4}(Co_5)Si_8O_{22}(OH)_2$	Fine fibers (pink). Partial entry of Co^{+2} into X position
4	(0.5Mg + 0.5Co):3:2:0	700°, 3000 atm., 6 hr.	$Na_{2.2}H_{0.2}(Mg_{3.0}Co_{2.8})Si_8O_{22}(OH)_2$	Relatively coarse, weak fibers. Low extra protons. Partial Mg(Co) in X position
5	(0.5Mg + 0.5Fe):2:2:0	600°, 3000 atm., 6 hr.	...	Very fine amphibole fibers, light gray-green
6	1(Mg):2:3:6	700°, 3000 atm., 6 hr.	$Na_{1.74}H_{0.65}Mg_{0.7}(Mg_5)Si_8O_{22}(F_{1.27})(OH)_{0.73}$	Incomplete F subst. for (OH). Mg in X position

[a] Expressed as moles of divalent cation (as hydroxide):moles of SiO_2:moles "free" NaOH:moles of F^- (as NaF). [b] Based on 8 Si atoms. H content (above $2(OH)^-$:8Si) calculated.

TABLE II

X-RAY DIFFRACTION DATA FOR SODIUM MAGNESIUM AMPHIBOLE[a]

d, Å.	I/I_0	d, Å.	I/I_0
8.39	41	2.32	29
4.81	31	2.28	26
4.51	41	2.25	30
4.04	21	2.23	51
3.85	34	2.08	18
3.41	62	1.70	36
3.28	45	1.57	21
3.15	64	1.52	17
2.99	41	1.50	31
2.92	17	1.44	25
2.82	19	1.39	16
2.72	100	1.31	15
2.58	37	1.29	19
2.51	81		

[a] Values of d for lines with I/I_0 less than 0.15 not reported (Cu Kα radiation).

TABLE III

SODIUM-MAGNESIUM AMPHIBOLE PROPERTIES

Fiber Properties	
Width, μ	0.01–5
Surface area, m.^{2}/g.	11
Density, 25°/4°	3.06
Crystal structure	Monoclinic
Tensile strength, p.s.i.	150,000–180,000
Refractive index	1.60–1.62
Chemical and Thermal Stability	
25% NaOH—2 hr. reflux	0–<0.5% loss
25% HCl—2 hr. reflux	7–9% loss
Diff. thermal anal.	348° (exotherm)
Thermograv. anal.	2% wt. loss at 740° 4% wt. loss at 840°

tained on the "fiber repeat distance" by aligning a bundle of fibers carefully and utilizing a rotation camera. A structure study of a sample of a Na–Co amphibole[21] has also been completed and will be published separately. This study was possible since relatively coarse needle-like fibers (10 μ diameter) could be obtained from the Na^+–Co^{+2}–SiO_2 system. Table II summarizes the X-ray diffraction powder pattern data for the sodium magnesium amphibole (example 1, Table I).

The amphibole powder data may be indexed as belonging to the monoclinic system (C2/m), with a = 9.89, b = 18.05, c = 5.28 Å., and β = 103°.

Properties of the Fibrous Sodium–Metal(II) Silicates. Crystal Habit.—All of the amphiboles described herein crystallized from the hydrothermal menstruum as well-defined, single crystal fibers. The fibers varied in thickness from 0.2 to 10 μ, with the majority in the 1–2 μ range. Extremely intertangled, spongy masses of fibers were removed from the synthesis capsules when a relatively small amount of water was present; more dilute systems resulted in much looser, more open fiber batts, still severely intergrown. This tangling causes difficulty in determining the maximum fiber length, but lengths of at least 4 in. have been found.

A distinguishing characteristic of all of the fine sodium magnesium amphiboles prepared in this study was the remarkable flexibility of the fibers when subjected to severe bending stresses. The fineness of individual fiber crystals precluded quantitative evaluation on conventional flex-test equipment, but qualitative comparision with other inorganic fibers could be gained by simply rolling small fiber clumps between the finger tips. In this crude test, the sodium amphibole fibers formed a stable "pill," whereas materials such as long-staple chrysotile asbestos and glass fibers suffered rapid attrition to a powder. Naturally occurring amphiboles, such as tremolite $[Ca_2Mg_5(Si_4O_{11})_2(OH)_2]$, also appear to be more brittle than the synthetic sodium amphiboles. The increased flex strength of the latter may be caused at least partially by the presence of a degree of hydrogen bonding between the silicate chains. The exact location of protons which enter the structure to preserve electrical neutrality has not been defined.

Stability.—Sodium magnesium amphiboles decrease 2.5–5% in weight on heating at 1000°. Long heating at 600° and short excursions to 660° leave the fibers

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(21) C. T. Prewitt, presented at the Annual Meeting of the American Mineralogical Society, New York, N. Y., Nov. 18, 1963.

essentially unchanged, but at 700° the structure slowly degenerates to a brittle pseudo-fibrous form of enstatite. The fluoride-substituted materials are somewhat more thermally stable, retaining their properties well at 920°.

Chemically the fibers are very resistant to hot concentrated base, but are slowly attacked by acid. In a study of the nature of acid-treated fiber, essentially no change was found in the stoichiometry of treated batts, indicating that the entire silicate structure is taken into solution. Table III gives some of the properties which have been determined.

Contribution from the Department of Chemistry,
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A Test of the Mulliken–Wolfsberg–Helmholz LCAO–MO Treatment of Metal Complexes[1a]

By F. A. Cotton[1b] and T. E. Haas[1c]

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The d-orbital splittings in $[Cr(NH_3)_6]^{3+}$, $[Co(NH_3)_6]^{3+}$, $[Co(NH_3)_6]^{2+}$, and $[Ni(NH_3)_6]^{2+}$ have been calculated by the type of LCAO–MO treatment originally suggested by Mulliken and first applied to complexes by Wolfsberg and Helmholz. The calculations were made in order to determine whether good results could be obtained for a variety of systems by adhering to a fixed set of rules for the choice of atomic orbital energies and a fixed value for the proportionality constant relating resonance integrals, H_{ij}, to the product of the overlap integral, S_{ij}, and the geometric mean of the integrals, H_{ii} and H_{jj}. The results show that strict adherence to such rules failed to afford uniformly accurate results.

Introduction

A reliable semiempirical method of calculating orbital energies for complexes of transition metals is obviously greatly to be desired. Two possible avenues to such a method have been proposed and utilized in individual instances, but their general reliability and applicability remain to be tested. The first of these is the point charge (or point dipole) electrostatic model. Some recent examples of its elaboration and use are provided by the work of Maki[2] and of Fenske, Martin, and Ruedenberg.[3] Because a model which treats ligand atoms as point charges is devoid of physical validity,[4–6] we do not believe that further studies of it offer promise of ultimate success.

The second approach utilizes the LCAO–MO method implemented by the assumptions of (1) a proportionality between resonance integrals and overlap integrals and (2) the equality of coulomb integrals and the corresponding valence state ionization potentials (VSIP) of atoms. The essentials of this approach were first introduced by Mulliken[7] and reduced to practice for some transition metal complexes by Wolfsberg and Helmholz.[8] The rationale and procedures for using VSIP's have been given by Moffitt.[9]

In the past few years several interesting applications of the Mulliken–Wolfsberg–Helmholz (MWH) method have been reported.[10] One which very clearly exemplifies the *modus operandi* and also gives excellent results is Ballhausen and Gray's treatment of vanadyl complexes.[11] However, the question naturally arises whether the treatment can be extended, unmodified, to other systems with comparable success. Especially interesting is whether the proportionality constant appearing in the relationship between overlap integrals and resonance integrals can be kept the same for various metal ions (say, all those of the first transition series) or whether it will be necessary to make what might be euphemistically called "judicious adjustments" from case to case. Specifically, we have formulated these questions: (1) How accurately can orbital energy differences be calculated using the MWH method *without* any *ad hoc* adjusting of either the VSIP's or the proportionality constant in the relationship between overlap integrals and resonance integrals? (2) How sensitive are the results to variations in these parameters?

Our attempt to answer these questions has consisted of the computation of Δ values for several $[M(NH_3)_6]^{n+}$ complexes and comparison of the results with the experimentally known Δ values. This sort of problem is one of the simplest and most important and should therefore constitute a fair and minimum test of the value of the method.

Procedure

The complexes selected for treatment are $[Cr(NH_3)_6]^{3+}$, $[Co(NH_3)_6]^{3+}$, $[Co(NH_3)_6]^{2+}$, and $[Ni(NH_3)_6]^{2+}$. Ammines were chosen so that metal–ligand π interactions could be ignored. Metal ions of the first transition series were selected because

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[1] (a) Supported by the U. S. Atomic Energy Commission. (b) Fellow of the Alfred P. Sloan Foundation. (c) National Science Foundation Predoctoral Fellow.

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