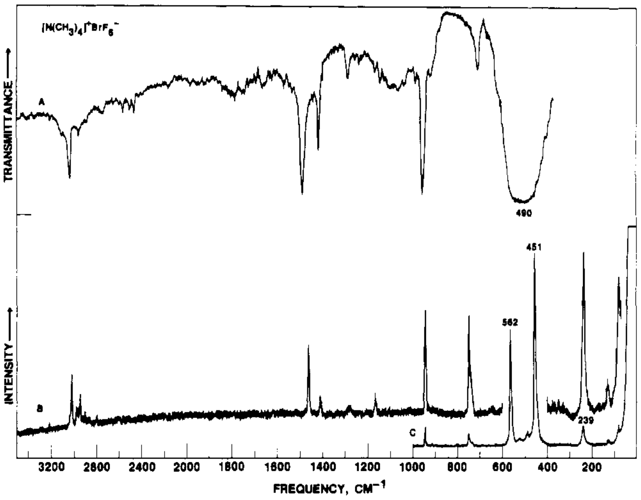

Figure 3. Vibrational spectra of solid $[N(CH_3)_4]BrF_6$.

$[N(CH_3)_4]^+BrF_4^-$ salt have also been prepared and characterized.

Acknowledgment. We are grateful to Dr. C. J. Schack and R. D. Wilson for their help and to the Air Force Astronautics Laboratory, Edwards AFB, for financial support.

Registry No. $[N(CH_3)_4]ClF_4$, 122821-59-4; $[N(CH_3)_4]F$, 373-68-2; $CsClF_4$, 15321-04-7; $[N(CH_3)_4]BrF_4$, 122821-60-7; $CsBrF_4$, 15705-88-1; $[N(CH_3)_4]BrF_6$, 35064-02-9; $CsBrF_6$, 26222-92-4.

Contribution from Rocketdyne, A Division of Rockwell International Corporation, Canoga Park, California 91303

Anion Exchange in NF_4^+ Salts Using Graphite Salts as an Oxidizer- and Acid-Resistant Anion-Exchange Medium

Karl O. Christe* and Richard D. Wilson

Received May 19, 1989

Although a large number of NF_4^+ salts are presently known,[1] only two of these salts, NF_4SbF_6[2] and NF_4BiF_6,[3] are readily accessible by direct synthesis from NF_3, F_2, and the corresponding Lewis acid at elevated temperatures and pressures. Since the SbF_6^- and BiF_6^- anions are heavy and do not significantly contribute to the performance of these salts in applications such as NF_3–F_2 gas generators[4] and energetic formulations,[5] it is necessary to replace the SbF_6^- anion in NF_4SbF_6 by lighter and/or more energetic anions.[4] In the past, this has been achieved mainly by a metathetical exchange of the anion at low temperature in anhydrous HF or BrF_5 as a solvent.[6]

$$NF_4SbF_6 + CsBF_4 \rightarrow CsSbF_6\downarrow + NF_4BF_4 \qquad (1)$$

The main drawbacks of reaction 1 include the following: the purity of the resulting NF_4BF_4 is only about 92%, unless repeated recrystallizations from HF and BrF_5 solutions are used;[2] the yields of NF_4BF_4 are less than quantitative (typically ~80%, due to losses during the recrystallizations and hold up of mother liquor on the filter cake); and the process is a batch process that requires troublesome low-temperature filtration steps involving anhydrous HF or BrF_5 solutions. It was, therefore, desirable to develop an improved process for exchanging the anion in NF_4SbF_6, which ideally would result in quantitative yields and high purities of the desired NF_4^+ salts in a simple, one-step process under ambient conditions. In this paper we describe such a process that had been discovered in our laboratory 8 years ago but could not be reported earlier due to the classification of a patent.[7]

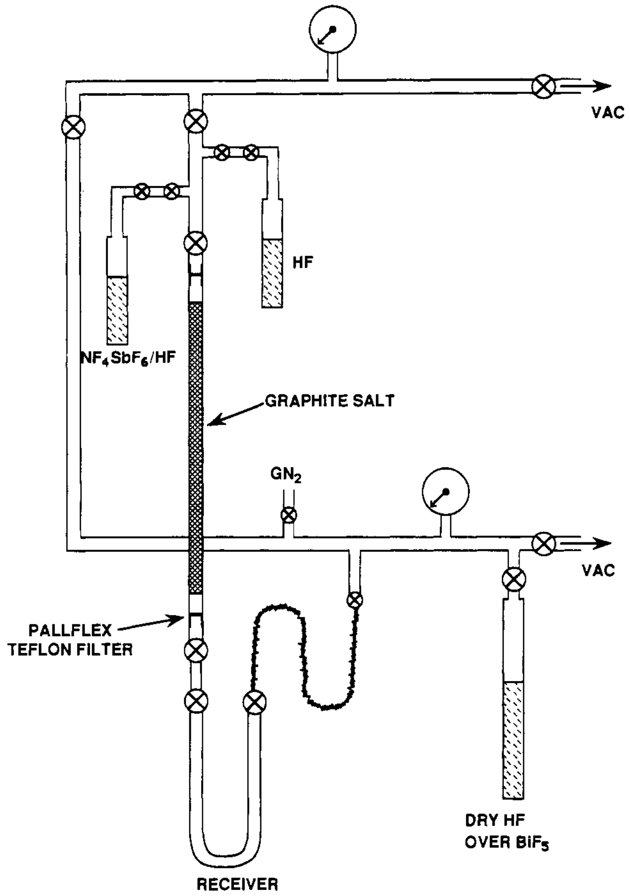

Figure 1. Apparatus used for the ion-exchange reactions between graphite salts and NF_4SbF_6.

Experimental Section

Starting Materials. Three different types of graphite were used in the course of this study. The first one consisted of spectrographic graphite (SG) electrodes, manufactured by the National Carbon Co., a Division of Union Carbide. The second one was a pyrolytic graphite (PG) slab for use in rocket nozzles, obtained from Hercules, and the third one was highly oriented pyrolytic graphite (HOPG) with a mirrorlike surface, obtained from Union Carbide by courtesy of Dr. A. Moore. All three types of graphite were ground in a mortar, classified according to particle size by the use of sieves, dried in a dynamic vacuum at 300 °C, and treated with 2 atm of F_2 pressure at room temperature for several hours prior to their use.

Hydrogen fluoride (Matheson) was dried by storage over BiF_5.[8] Arsenic pentafluoride (Ozark Mahoning), BF_3 and PF_5 (Matheson) were purified by fractional condensation prior to their use. The F_2 (Air Products) was passed through a NaF scrubber for removal of any HF. The preparations of NF_4SbF_6[6] and O_2AsF_6[9] have previously been described. The SO_2ClF (Ozark Mahoning) was pretreated at −78 °C with $O_2^+AsF_6^-$, followed by fractional condensation in a dynamic vacuum through a series of −78, −112, and −196 °C traps, with the material retained at −112 °C being used.

Caution! Anhydrous HF causes severe burns. Elemental fluorine and NF_4^+ salts are strong oxidizers and must be handled with the safety precautions previously described.[6]

Apparatus. Volatile materials were handled in stainless-steel–Teflon–FEP vacuum lines as previously described.[10] Nonvolatile materials

---

(1) For a recent review on NF_4^+ chemistry see: Nikitin, I. V.; Rosolovskii, V. Ya. *Russ. Chem. Rev.* (*Engl. Transl.*) **1985**, *54*, 426.

(2) Christe, K. O.; Schack, C. J.; Wilson, R. D. *J. Fluorine Chem.* **1976**, *8*, 541 and references cited therein.

(3) Wilson, W. W.; Christe, K. O. *J. Fluorine Chem.* **1988**, *40*, 59 and references cited therein.

(4) Christe, K. O.; Wilson, W. W. *Inorg. Chem.* **1982**, *21*, 4113 and references cited therein.

(5) Christe, K. O. U.S. Pat. 4,207,124, 1980.

(6) Christe, K. O.; Wilson, W. W.; Schack, C. J.; Wilson, R. D. *Inorg. Synth.* **1986**, *24*, 39.

(7) Christe, K. O. U.S. Pat. 4,683,129, 1987.

(8) Christe, K. O.; Wilson, W. W.; Schack, C. J. *J. Fluorine Chem.* **1978**, *11*, 71.

(9) Shamir, J.; Binenboym, J. *Inorg. Chim. Acta* **1968**, *2*, 37.

were handled in the dry nitrogen atmosphere of a glovebox. The ion-exchange reactions were carried out in a specially built apparatus (see Figure 1), constructed from injection-molded Teflon–PFA tubes, valves, and fittings (Fluoroware). The exchange column consisted of a 40 cm long, $^3/_8$ in. o.d. heavy-wall Teflon–PFA tube and was packed with the graphite salt to a height of about 35 cm. The column packing was held in place at both ends by porous Teflon filter disks (Pallflex). Pure HF and an HF solution of NF_4SbF_6 were stored in two $^1/_2$ in. o.d. Teflon ampules attached at right angles to the Teflon manifold directly above the exchange column. These ampules could be rotated about their horizontal tube sections connecting them to the manifold, thereby allowing either neat HF or HF–NF_4SbF_6 solutions to be added to the top of the column. To overcome the resistance of the Teflon filters, the apparatus could be either pressurized with several atmospheres of dry gaseous N_2 or evacuated. The bottom of the exchange column was connected to a detachable $^3/_4$ in. o.d. Teflon U-trap receiver, equipped with two Teflon valves and attached with Teflon flex tubing (Penntube) to the vacuum manifold.

Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrometer, and Raman spectra, on either a Spex Model 1403 instrument with 647.1-nm excitation or a Cary Model 83 instrument with 488-nm excitation. X-ray powder patterns were taken with a General Electric Model XRD-6 diffractometer, Ni-filtered Cu Kα radiation, and a 114.6 nm diameter Philips Norelco camera on powder samples in sealed 0.5-mm quartz capillaries.

Synthesis of Graphite Salts. C_nBF_4. All the graphite BF_4 salts were prepared by the method of Nikonorov[11] from graphite and a 2:1 molar mixture of BF_3 and F_2 at 2 atm pressure in a Monel cylinder at room temperature until no further weight uptake occurred. The initial BF_3–F_2 uptake by the graphite was rapid and exothermic for the pyrolytic graphite samples. After three 3-h exposures to BF_3–F_2 mixtures, followed each time by pumping on the sample for several hours at room temperature for the removal of loosely intercalated BF_3 and F_2, no further BF_3–F_2 uptake was observed. The value of n was determined from both the weight increase of the solids and the amounts of unreacted BF_3 and F_2 recovered, with both values generally being in excellent agreement. For the different types of graphite used in our study, the following compositions were obtained:

spectrographic graphite (SG)	$C_{11.12}{}^+BF_4{}^-$
pyrolytic graphite (PG)	$C_{8.10}{}^+BF_4{}^-$
highly oriented pyrolytic graphite (HOPG)	$C_{8.10}{}^+BF_4{}^-$

The PG and HOPG salts were shown by X-ray diffraction to be first-stage intercalates with a_0 = 2.46 Å and c_0 = 7.69 Å, in excellent agreement with previous literature values.[12,13]

C_nAsF_6. For the syntheses of graphite AsF_6 salts, two different methods were used. The first one was that of Nikonorov[11] and has been described above for C_nBF_4. With the different types of graphite, this method resulted in the following compositions:

spectrographic graphite (SG)	$C_{11.60}AsF_6$
pyrolytic graphite (GP)	$C_{9.83}AsF_6$
highly oriented pyrolytic graphite (HOPG)	$C_{9.70}AsF_6$

The second method was that of Bartlett and co-workers[14] which involved the oxidation of spectrographic graphite by O_2AsF_6 in SO_2ClF, first at −60 °C and then at room temperature. On the basis of the observed material balance, the final product had the composition $C_{8.72}AsF_6$.

All the C_nAsF_6 salts were first-stage intercalates with a_0 = 2.45 and c_0 = 7.87 Å, in excellent agreement with previous reports.[15,16]

C_nPF_6. For the synthesis of C_nPF_6, the method of Nikonorov[11] and the use of pyrolytic graphite resulted in a first-stage intercalate having the composition $C_{12.40}PF_6$ and repeat distances of a_0 = 2.45 Å and c_0 = 7.69 Å, in reasonable agreement with a previous report.[12]

Attempts to prepare C_nPF_6 by a displacement reaction at ambient temperature between $(PG)C_{8.1}BF_4$ and 4-fold excess of PF_5, in a stainless-steel cylinder of a small enough volume to result in a liquid PF_5 phase (vapor pressure of PF_5 at 21.1 °C = 28.2 atm) resulted in a product having the molar composition $0.493C_{8.1}BF_4{\cdot}0.507C_{12.5}PF_6$, as shown by the weight change of the solid and the amounts of PF_5 consumed and BF_3 liberated. A second treatment with PF_5 for more than 6 months under identical conditions, followed by removal of the volatile material at 50 °C, resulted in very little additional PF_5 uptake but an evolution of some BF_3, indicating that the $C_{8.1}BF_4$ may have contained, in addition to $BF_4{}^-$, some intercalated BF_3.

Preparation of NF_4BF_4 by Ion Exchange. In a typical experiment, 6.096 g (33.12 mmol) of $(PG)C_{8\cdot10}BF_4$ having a particle size of 35 mesh was loaded inside the drybox into the Teflon exchange column. The column was attached to the Teflon manifold and wet with anhydrous HF. A Teflon ampule was loaded in the drybox with 1.094 g (3.357 mmol) of NF_4SbF_6 and attached to the Teflon manifold, and anhydrous HF (12 mL of liquid) was condensed into the ampule at −78 °C. The resulting HF solution of NF_4SbF_6 was slowly passed over a 1-h time period through the $C_{8.1}BF_4$ column, followed by a rinse with about 10 mL of anhydrous HF. The eluents were collected in the Teflon receiver U-tube and pumped to dryness at 50 °C. The white solid residue (573 mg; weight calculated for 3.357 mmol of NF_4BF_4 = 593 mg, 97% yield) was shown by infrared and Raman spectroscopy to be pure NF_4BF_4.[17]

Similarly, a sample of 4.91 mmol of NF_4SbF_6, when slowly passed through a column of 14.0 mmol of $(SG)C_{11.12}BF_4$, produced 3.78 mmol (77% yield) of pure NF_4BF_4.

Preparation of NF_4AsF_6 by Ion Exchange. In a typical experiment, 3.05 mmol of NF_4SbF_6, when passed through a column of 28.7 mmol of $(PG)C_{9.83}AsF_6$, produced 3.05 mmol (100% yield) of spectroscopically pure NF_4AsF_6.[17]

Similarly, a sample of 5.0 mmol of NF_4SbF_6, when passed through a column of 7.84 mmol of $(SG)C_{8.7}AsF_6$, resulted in 3.6 mmol of NF_4AsF_6 and 1.4 mmol of NF_4SbF_6.

Preparation of NF_4PF_6 by Ion Exchange. When a solution of 3.27 mmol of NF_4SbF_6 in anhydrous HF was passed through a column packed with 23.8 mmol of $(PG)C_{12.4}PF_6$, the eluted product consisted of 1.49 mmol of NF_4PF_6 and 0.49 mmol of NF_4SbF_6.

Results and Discussion

A metathetical reaction of the type

$$A^+B^- + C^+D \rightarrow AD\downarrow + C^+B^- \qquad (2)$$

is in principle a simple ion exchange in which the purity of the desired product is governed by the solubility products of the four salts involved. For this process to work efficiently, the solubility product of AD must be much smaller than those of the three remaining salts. Since this is not the case for reaction 1, low-temperature filtrations and multiple recrystallizations from anhydrous HF and BrF_5 are required that lower the yields. The solubility problem with AD might be overcome by making A^+ an insoluble, polymeric, stationary phase. This principle is well-known and is widely used in ion-exchange resins. Since the metathetical NF_4BF_4 process (1) is a simple anion exchange, it could be improved upon by replacing $CsBF_4$ with a $BF_4{}^-$ salt of a cationic resin that is stable toward both anhydrous HF and the strongly oxidizing $NF_4{}^+$ cation. Although acid- and oxidizer-resistant cation exchangers, such as Du Pont's Nafion, are well-known, no corresponding anion exchangers were available.

Attempts were made to utilize the cation exchanger Nafion (XR resin from Du Pont which is a copolymer of tetrafluoroethylene and perfluoro-4-methyl-3,6-dioxa-7-octenesulfonic acid) for the preparation of NF_4BF_4 according to (3) and (4). Although small

$$R_fSO_3{}^-Na^+ + NF_4{}^+SbF_6{}^- \rightarrow R_fSO_3{}^-NF_4{}^+ + Na^+SbF_6{}^- \qquad (3)$$

$$R_fSO_3{}^-NF_4{}^+ + Na^+BF_4{}^- \rightarrow R_fSO_3{}^-Na^+ + NF_4{}^+BF_4{}^- \qquad (4)$$

amounts of $NaSbF_6$ were detectable in the eluent of (3), treatment of the resulting solid with a $Na^+BF_4{}^-$ solution did not show any evidence for NF_4BF_4.

In our search for a suitable acid- and oxidizer-resistant anion-exchange medium, it was discovered that graphite salts are well suited for this purpose. Since the syntheses and properties of graphite salts are the subject of considerable controversy, our results on the preparation of these salts will be briefly summarized before presenting our data on the actual ion exchange reactions.

---

(10) Christe, K. O.; Wilson, W. W.; Schack, C. J. *Inorg. Synth.* **1986**, *24*, 3.

(11) Nikonorov, Yu. I. *Kinet. Katal.* **1979**, *20*, 1598.

(12) Rosenthal, G. L.; Mallouk, T. E.; Bartlett, N. *Synth. Met.* **1984**, *9*, 433.

(13) Brusilovsky, D.; Selig, H.; Vaknin, D.; Ohana, I.; Davidov, D. *Synth. Met.* **1988**, *23*, 377.

(14) Bartlett, N.; McQuillan, B.; Robertson, A. S. *Mater. Res. Bull.* **1978**, *13*, 1259.

(15) Bartlett, N.; McCarron, E. M.; McQuillan, B. W. *Synth. Met.* **1979/80**, *1*, 221.

(16) McCarron, E. M. Ph.D. Thesis, University of California, Berkeley, CA, 1981, 58.

(17) Christe, K. O.; Schack, C. J.; Wilson, R. D. *Inorg. Chem.* **1976**, *15*, 1275.

Syntheses of Graphite Salts. In our study different types of graphite starting material were used, i.e. spectrographic graphite (SG) and two kinds of pyrolytic graphite (PG), one from a graphite slab used for rocket nozzle cones, and the second one from highly oriented, mirror-surfaced graphite pieces. The pyrolytic graphites are more highly graphitized, better oriented, and more easily intercalated than the spectrographic graphite and, therefore, have been used almost exclusively in the previously reported studies.[11-13]

In agreement with the previous studies,[11-13] the reaction

$$nC + 0.5F_2 + BF_3 \rightarrow C_n^+BF_4^- \qquad (5)$$

yielded a first-stage intercalate with n being very close to 8.0 and the same identity period. No particular effort was made in this study to determine whether in C_8BF_4 the boron is present exclusively as BF_4^- or if there might also be some free BF_3 and/or F_2 present.[13] It should be noted, however, that the addition of neat anhydrous HF to the (PG)- and (HOPG)C_8BF_4 generally resulted in gas evolution and a very pronounced swelling of the graphite salt, indicating the possible intercalation of some free BF_3.

For the synthesis of $C_n^+AsF_6^-$, the direct synthesis from graphite, AsF_5, and F_2 yielded for the two pyrolytic graphites n values close to 9.8 and for spectrographic graphite a value of 11.6. With $O_2^+AsF_6^-$ used as the oxidant[14] and spectrographic graphite

$$nC + O_2^+AsF_6^- \rightarrow C_n^+AsF_6^- + O_2 \qquad (6)$$

a composition of $C_{8.7}AsF_6$ was obtained. These salts were first-stage intercalates and approach the limiting composition C_8AsF_6, which has a close packing of the AsF_6^- anions in the galleries.[18] For C_nPF_6, the direct synthesis using pyrolytic graphite, PF_5, and F_2 produced a first-stage intercalate having the composition $C_{12.4}PF_6$. The fact that the limiting composition for C_nPF_6 appears to be about $C_{12}PF_6$, while that for C_nAsF_6 is about C_8AsF_6, cannot be due to steric effects because PF_6^- is smaller than AsF_6^-. It has been attributed[19] to the lower fluoride ion affinity of PF_5 relative to that of AsF_5. It, therefore, appears that PF_6^- cannot support a positive charge on carbon higher than that corresponding to a composition of about C_{12}^+. Further evidence for the limiting composition of C_nPF_6 being about $n = 12$ was obtained by a displacement reaction between (PG)$C_{8.1}BF_4$ and liquid PF_5 at room temperature. Although only half of the BF_3 was displaced by PF_5 in a single treatment, the stoichiometry of the displacement reaction was such that 1 mol of PF_5 liberated 1.54 mol of BF_3; i.e., the $C_{8.1}BF_4$ was converted to $C_{12.5}PF_6$ and BF_3. The $C_{12.5}PF_6$ composition observed for this displacement reaction is in excellent agreement with that of $C_{12.4}PF_6$ derived from the direct synthesis from graphite, PF_5, and F_2 (see above). It is noteworthy that the stoichiometry of the above displacement reaction resembles that previously observed for the $C_7SO_3F + AsF_5$ system.[20]

In conclusion, our syntheses of graphite salts are in good agreement with the previous literature data suggesting limiting compositions of about C_8BF_4, C_8AsF_6, and $C_{12}PF_6$ for these first-stage intercalates.

Ion-Exchange Reactions. Solutions of NF_4SbF_6 in HF, when passed through columns of either C_8BF_4 or C_8AsF_6, readily exchange the SbF_6^- anion for either BF_4^- or AsF_6^-.

$$C_8BF_4 + NF_4SbF_6 \rightarrow C_8SbF_6 + NF_4BF_4 \qquad (7)$$

$$C_8AsF_6 + NF_4SbF_6 \rightarrow C_8SbF_6 + NF_4AsF_6 \qquad (8)$$

In this manner, spectroscopically pure NF_4BF_4 or NF_4AsF_6 can be prepared. It is important to use a suitable column geometry, i.e. a large height to diameter ratio, and a sufficient molar excess of the graphite salt. The importance of the column geometry and of flow conditions was demonstrated by an experiment whereby a sample of (PG)$C_{8.1}BF_4$ was stirred with a large excess of NF_4SbF_6 dissolved in HF. Even after a contact time of 10 h, only an insignificant anion exchange had occurred. The importance of using a sufficient excess of graphite salt over NF_4SbF_6 was demonstrated in an experiment where the mole ratio of $C_{8.7}AsF_6$ to NF_4SbF_6 was only 1.57. In this case the conversion of NF_4SbF_6 to NF_4AsF_6 was only 72 mol %.

Another important point is that the graphite salt starting material is fully oxidized to a C_8^+ stage. If the graphite salt is not completely oxidized, it will be oxidized by NF_4SbF_6 in a reaction, analogous to (6), resulting in the loss of NF_4^+ values.

$$8C + NF_4^+SbF_6^- \rightarrow C_8^+SbF_6^- + NF_3 + 0.5F_2 \qquad (9)$$

This point was demonstrated in several experiments using C_nBF_4 compositions in which n ranged from 14 to 16 and the yields of NF_4BF_4 were less than quantitative.

For the synthesis of NF_4PF_6, the most highly oxidized graphite PF_6 salt available was $C_{12.4}PF_6$. In view of the incomplete oxidation state of the graphite, it was not surprising that a 40 mol % loss of NF_4^+ values occurred during the exchange reaction.

Conclusion. Graphite salts can be used as anion-exchange resins that are highly resistant toward strong acids and oxidizers. To our knowledge, these are the first anion exchangers capable of withstanding such harsh conditions for which previously only cation exchangers, such as Nafion, were available. The usefulness of graphite salts as anion exchangers was demonstrated by an improved method for the production of advanced NF_4^+ salts. This method eliminates most of the drawbacks of the previously used low-temperature, metathetical process[6] and provides the desired NF_4^+ salts in high purities and yields by a simple, one-step process under ambient conditions.

Acknowledgment. We are indebted to Drs. C. J. Schack and W. W. Wilson for their help, to Dr. A. Moore for a sample of HOPG graphite, and to the Office of Naval Research and the U.S. Army Research Office for financial support.

---

(18) Bartlett, N.; McQuillan, B. W. In *Intercalation Chemistry*; Wittingham, M. S., Jacobson, A. J., Eds.; Academic Press: New York, 1982.

(19) Hagiwara, R.; Lerner, M.; Bartlett, N. Presented at the ACS Ninth Winter Fluorine Conference, St. Petersburg, FL, Feb 1989; paper 63.

(20) Karunanithy, S.; Aubke, F. *J. Fluorine Chem.* **1984**, 25, 339.

Contribution from Ames Laboratory-DOE[1]
and Department of Chemistry,
Iowa State University, Ames, Iowa 50011

Synthesis and Structure of the Zintl Phase K_2SiAs_2

Weir-Mirn Hurng, Eric S. Peterson, and John D. Corbett*

Received April 14, 1989

Binary, ternary, and higher compounds of the main-group elements afford a remarkable versatility in the compositions and structures that can be achieved in the so-called Zintl (valence) phases. The earliest considerations of this type of compound dealt with the close relationship perceived between the anions in these and the isosteric, isoelectronic units found for the elements. The parent member was NaTl in which Tl^- in the diamond structure was thought to be analogous to, in particular, elemental Si, Ge, and (gray) Sn.[2] Further relationships of this sort included the very similar anion vs element structure connectivities and bonding in $CaSi_2 \hat{=} As$, $NaSi \hat{=} P_4$ and $NaSb \hat{=} Te$.[3] Since then, many marvelous anionic networks, oligomers, and clusters have been discovered in which the same simple valence (octet) principles are operational but which cannot be realized in the structures of the

---

(1) Ames Laboratory-DOE is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This research was supported by the Office of Basic Energy Sciences, Materials Sciences Division.

(2) Zintl, E.; Woltersdorf, G. *Z. Elektrochem.* **1935**, *41*, 876.

(3) Klemm, W.; Busmann, E. *Z. Anorg. Allg. Chem.* **1963**, *319*, 297.