about 0.1°K for cubic tungsten bronzes. Similarly, no superconductivity was observed in this Na$_{0.96}$WO$_3$ phase down to 1.3°K, the lower limit of our measurement.

Sn$_x$WO$_3$.—The group IVa metal tungsten bronze Pb$_x$WO$_3$ with tetragonal structure has been prepared by the melt–fusion technique.[9] Hexagonal Sn$_x$WO$_3$ was obtained hydrothermally by the reaction of 2 g of an SnO–WO$_3$–W mixture in a 3:9:1 mole ratio in 3 ml of H$_2$O at 400° for 8 hr. Blue–black microcrystals of composition Sn$_{0.21}$WO$_3$ (Calcd: Sn, 9.71. Found: Sn, 9.72) were formed. Reaction of 5.8 g of an SnO–WO$_3$–W mixture in a 3:1:1 mole ratio in 1 ml of H$_2$O at 700° for 10 hr gave single crystals of hexagonal Sn$_{0.24}$WO$_3$ (Calcd: Sn, 10.94. Found: Sn, 11.10) of sufficient size to demonstrate their metallic-type conduction (Table I). These Sn$_x$WO$_3$ compounds showed no superconducting transition, T_c, down to the lowest measured temperature of 1.3°K, even after an etch with strong acid which has been demonstrated to increase T_c.[10]

Hexagonal Sn$_x$WO$_3$ was also obtained as very small blue–black crystallites by the solid-state reaction of 5 g of an SnO–WO$_3$–W mixture in a 3:9:1 mole ratio in a sealed, evacuated silica tube at 1000° for 24 hr. Crystals of WO$_2$ contaminated this phase. Again, no superconductivity was noted to 1.3°K. When the same reactants were heated for 5 days at 1000°, purple needles of Sn$_x$WO$_3$ having the tetragonal bronze structure (tunnel-type) as in Pb$_x$WO$_3$ rather than the hexagonal type were obtained. After extraction with hot 40% H$_3$PO$_4$, a composition Sn$_{0.19}$WO$_3$ (Calcd: Sn 8.86. Found: Sn, 8.95) was obtained. As with the hexagonal Sn bronzes, no superconductivity was observed to 1.3°K.

Results and Disscusion

Cell dimensions and electrical properties of the complete group of alkali metal tungsten bronzes are summarized in Table I for comparative purposes. The near equivalence of these metallic materials reflects the importance of the WO$_6$ octahedral framework in establishing their basic properties. Goodenough[11] has proposed that if the coordination of oxygen is less than four, a π^* band may be formed using the metal d orbitals and oxygen orbitals with π^*-bonding symmetry. Since oxygen atoms are coordinated by two tungsten atoms in all of the tungsten bronze structure types, this band is possible. The band is empty in WO$_3$ but has electrons donated to it, *e.g.*, by an alkali metal, in the various tungsten bronzes.

Transitions to the superconducting state in the range 1–6°K have now been observed in hexagonal tungsten bronzes containing all of the alkali metals, as well as the group IIa and IIIa metals Ca, Sr, Ba, In, and Tl.[5] The absence of a similar transition in the analogous metallic, hexagonal Sn$_x$WO$_3$ compositions of group IVa thus seems unusual. Since our lower limit of measurement is approximately 1.3°K, we cannot rule out superconductivity occurring in these Sn bronzes at some lower temperature.

The existence of Li$_x$WO$_3$ with the hexagonal tungsten bronze structure is unusual in that Li would appear to be too small to be held in the large hexagonal tunnels. These tunnels would seem best suited for cations larger than ~1 Å in radius while Li is much smaller than this (R_{Li} ~ 0.68 Å). Other sites are available in the hexag-

onal tungsten bronze structure. The largest of these would be trigonal prisms capped on all rectangular faces. If the Li were at one end of a prism, its coordination to oxygen could be six or even three. Jamieson, *et al.*,[12] have suggested that Li occupies sites of this type in K$_{1-x}$Li$_x$NbO$_3$ (x ~ 0.4) compounds which have the tetragonal tungsten bronze structure.[13] Graham and Wadsley[14] have shown that the presence of large cations in the hexagonal tunnels is not structurally necessary since MoW$_{11}$O$_{36}$ and MoW$_{14}$O$_{45}$ both have the hexagonal tungsten bronze structure with these tunnels being completely empty.

Since Li$_x$WO$_3$ was prepared hydrothermally, it is also possible that hydrated Li is present in the hexagonal tunnels.

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Fluorinated Derivatives of Azodiformamidine

BY J. B. HYNES, T. E. AUSTIN, AND L. A. BIGELOW

It was recently reported that the stirred, solid fluorination of guanidine monohydrofluoride produced the novel compound pentafluoroguanidine, (NF$_2$)$_2$C=NF.[1] We wish to report that when azodiformamidine dinitrate was allowed to react with very dilute fluorine in the presence of sodium fluoride, a series of new highly fluorinated azo compounds was formed. The most abundant of these was difluorotetrakis(difluoramino)-azomethane, (NF$_2$)$_2$CFN=NCF(NF$_2$)$_2$, a faintly yellow liquid which boiled at 81°. Also isolated were two isomers of [bis(difluoramino)fluoromethylazo]trifluoroformamidine, (NF$_2$)$_2$CFN=NC(=NF)NF$_2$, IIa and b, and three isomers of hexafluoroazodiformamidine, NF$_2$C(=NF)N=NC(=NF)NF$_2$, IIIa, b, and c.

The colors of the unsaturated compounds varied from yellow-orange to red, owing to the effect of conjugation of the fluorimino group with the azo chromophore. Pertinent spectroscopic properties and probable stereochemical configurations for these materials are summarized in Table I. It should be pointed out that for

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Table I
Spectroscopic Properties and Tentative Structural Assignments for Fluorinated Derivatives of Azodiformamidine

Compd no.	Nmr chemical shifts relative to CFCl₃, ppm	Uv absorption max (vapor phase), mμ
I	$(NF_2)_2CN{=}NC(NF_2)_2$ −22.3 $\quad$ F $\quad$ F +141.6	386
IIa	F +142.2 $\quad$ −23.2 $(NF_2)_2C$ $\quad$ N=N $\quad$ F −9.2 $\quad$ C=N $\quad$ NF₂ −47.2	438
IIb	F +142.0 $\quad$ −24.0 $(NF_2)_2C$ $\quad$ N=N $\quad$ C=N $\quad$ −43.3 NF₂ $\quad$ F −22.0	424
IIIa	NF₂ $\quad$ N=C $\quad$ F $\quad$ N=N $\quad$ F −22.4 $\quad$ C=N $\quad$ NF₂ −45.7	465
IIIb	−20.3 F $\quad$ NF₂ −41.4 $\quad$ N=C $\quad$ N=N $\quad$ F −9.3 $\quad$ C=N $\quad$ NF₂ −45.6	455
IIIc	F $\quad$ NF₂ $\quad$ N=C $\quad$ N=N $\quad$ C=N $\quad$ −41.2 NF₂ $\quad$ F −19.1	452

each compound the approximate relative nmr peak areas were in accord with these assignments.

The unsaturated structures presented in Table I are in their planar conformations which should be their most stable ones since planarity permits maximum conjugation. Also, there was no evidence to indicate that any of these compounds possessed a *cis*-azo configuration.[2] Therefore, the isomerism presumably involves the location of the fluorimino fluorine with re-

(2) H. Zollinger, "Azo and Diazo Chemistry, Aliphatic and Aromatic Compounds," Interscience Publishers, Inc., New York, N. Y., 1961.

spect to the adjacent difluoroamino group. The *syn*- and *anti*-fluorimino fluorines of IIa and IIb were assigned by comparing their chemical shifts with that reported for $(NF_2)_2C{=}NF$ (−20.2 ppm).[1] For the latter compound, the fluorimino fluorine must be *syn* to an NF₂ group so it has been assumed here that values in the neighborhood of −20 ppm correspond to a *syn* configuration with respect to the neighboring NF₂ group, while values around −10 ppm indicate an *anti* arrangement. However, the value for IIIa is not consistent with this line of reasoning, and, therefore additional data are required before definite stereochemical assignments can be made. The *syn,anti* structure of IIIb is unequivocal, since its nmr spectrum shows the presence of two nonequivalent NF₂ groups and two nonequivalent fluorimino fluorines, the relative peak areas being in the ratio of 2:2:1:1, respectively.

Each of these materials is *highly explosive* as is the crude reaction mixture. However, they have been routinely handled and stored in a well-shielded high-vacuum system equipped with Teflon stopcocks. As a general rule, the unsaturated derivatives are more sensitive to shock and should be transported in an inert solvent such as $CF_2ClCFCl_2$ whenever possible.

Experimental Section

The infrared spectra were measured in the vapor phase using a Beckman IR-8 spectrophotometer. The chromatographic analyses were performed with a Microtek 1500 gas chromatograph while the molecular weights were determined by vapor density measurements. All operations involving these compounds were conducted behind movable ³/₈-in. Plexiglass shields.

The Fluorination of Azodiformamidine Dinitrate.—Azodiformamidine dinitrate was prepared by the permanganate oxidation of aminoguanidine nitrate or carbonate according to the method of Thiele.[3] It was obtained in a very finely divided state by dissolution in a minimum of dimethyl sulfoxide at room temperature and reprecipitation by the addition of an equal volume of anhydrous acetone. Both it and the sodium fluoride were vacuum dried over P₂O₅ before use.

An 8-oz Teflon FEP bottle equipped with Teflon inlet and exit tubes, the latter being attached to a trap immersed in a Dry Ice–trichloroethylene bath, was employed. The reactor was charged with 3 g of azodiformamidine dinitrate and 20 g of NaF which were stirred magnetically while being immersed in a −75° bath. Next, a flow of 10 cc/min of F₂ + 250 cc/min of N₂ was passed through the reactor, and after 1 hr the cold bath was replaced by an ice–water bath and the fluorination continued for 24 hr. The red-orange liquid condensate (0.8–1.0 ml) was then carefully diluted with an equal volume of CF₂ClCFCl₂ and transferred to a conical vessel for chromatographic analysis. The volatile products which passed through the −75° trap were numerous but the most abundant was FONO₂.

A semipreparative chromatographic column consisting of two straight 4-ft lengths of copper tubing with 0.5-in. o.d. connected in series by means of a 0.25-in. o.d. copper U tube was used for the separation of the fluorination products. It was operated at ambient temperature with a helium flow of 200 cc/min and it was packed with 20% Halocarbon 13-21 oil on 60–80 mesh Chromosorb P. Using this apparatus, 0.2–0.4-ml samples (50% product in CF₂ClCFCl₂) could be resolved readily. The purified compounds were trapped in Pyrex U tubes immersed in Dry Ice–trichloroethylene baths.

The composition of the liquid product was usually 50–70% I and 25–40% IIa and b, with considerable variation from one

(3) J. Thiele, *Ann.*, **270**, 39 (1892).

run to the next. The remainder of the product consisted of the isomers of III (2-5%) and several unidentified azides. Using an estimated average density for the crude product of 1.6 g/ml and an average molecular weight of 280, the approximate yield of high-boiling products ranged between 30 and 40%. Physical properties other than those presented in Table I are summarized below, the compounds being presented in order of increasing chromatogaphic retention time.

sym-Difluorotetrakis(difluoramino)azomethane, (NF₂)₂CFN=NCF(NF₂)₂.—Compound I was a faintly yellow liquid which melted between −75 and −78° and had a boiling point of 81°.[4] Its infrared spectrum exhibited principal absorptions located at 1366 (s), 1148 (m), 1016 (m), 980 (s), 952 (s), and 908 (s) cm⁻¹. The mass spectrum of (NF₂)₂CFN=NCF(NF₂)₂ gave the following peaks in order of decreasing relative intensity: 64 (CF₂N⁺), 31 (CF⁺), 52 (NF₃⁺), 83 (CF₂N⁺), 45 (CFN⁺), 135 (CF₅N₂⁺), 33 (NF⁺), 69 (CF₃⁺), 144 (CF₄N₄⁺), 50 (CF₂⁺), 12 (C⁺), 97 (CF₃N₂⁺), 26 (CN⁺), 54 (CN₃⁺), 76 (C₂N₃⁺), 125 (CF₅N₃⁺), 194 (C₂F₆N₄⁺), and 76 (C₂N₃⁺). Mol wt of C₂F₁₀N₆: calcd, 298; found, 306.

Photolysis of I using a 550-W high-pressure mercury lamp and a blue filter to remove radiation of wavelengths shorter than 330 mμ produced NF₂CF=NF, which was identified by its infrared spectrum.[5] Numerous degradation products such as CF₄, NF₃, and CF₂=NF were also formed and the Pyrex reaction bulb was severely etched.

[Bis(difluoramino)fluoromethylazo]trifluoroformamidine, (NF₂)₂CFN=NC(=NF)NF₂.—The isomer with the shorter retention time, IIa, was an orange liquid, bp 82°.[4] Its infrared spectrum exhibited bands centered at 1631 (w), 1272 (s), 1214 (m), 1124 (m), 1015 (m), 969 (s), 947 (s), 923 (s), 899 (s), 880 (s), 766 (m) cm⁻¹. The principal ions of its mass cracking pattern presented in order of decreasing relative intensity were: 31 (CF⁺), 64 (CF₂N⁺), 97 (CF₃N₂⁺), 52 (NF₂⁺), 83 (CF₃N⁺), 28 (N₂⁺), 135 (CF₅N₂⁺), 33 (NF⁺), 12 (C⁺), and 45 (CFN⁺). Mol wt of C₂F₈N₆: calcd, 260; found, 261.

The second isomer, IIb, was a yellow-orange liquid, bp 83°.[4] Its infrared spectrum, which was similar to that of its isomer, exhibited peaks at 1592 (w), 1272 (s), 1224 (m), 1124 (m), 1016 (s), 974 (s), 948 (s), 898 (s), and 766 (w) cm⁻¹. The mass spectrum showed the following peaks in order of decreasing relative intensity: 31 (CF⁺), 64 (CF₂N⁺), 52 (NF₂⁺), 97 (CF₃N₂⁺), 28 (N₂⁺), 83 (CF₃N⁺), 33 (NF⁺), 135 (CF₅N₂⁺), 12 (C⁺), and 45 (CFN⁺). Mol wt of C₂F₈N₆: calcd, 260; found, 258.

Hexafluoroazodiformamidine, NF₂C(=NF)N=NC(=NF)NF₂.—Compound IIIa was a deep red liquid which was very shock sensitive. The breaking of the liquid surface with an inverted capillary tube in preparation for its boiling point determination caused the sample to explode. Its infrared spectrum, which was almost identical with that of its isomer, IIIb, showed absorptions centered at 1618 (w), 1274 (w), 1220 (w), 1017 (m), 978 (m), 926 (s), 883 (s), and 752 (w), cm⁻¹. The values for IIIb were 1634 (w), 1284 (w), 1229 (w), 1013 (m), 980 (s), 926 (s), and 885 (s) cm⁻¹. The third isomer, IIIc, which was isolated only in trace amounts, had a very simple infrared spectrum with bands being located at 1587 (w), 1239 (w), 977 (s), and 889 (s) cm⁻¹. Mol wt of C₂F₆N₆ (IIIa): calcd, 222; found, 218.

(4) Siwoloboff method using an inverted capillary tube.

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Synthesis of New High-Pressure Pyrochlore Phases

BY R. D. SHANNON AND A. W. SLEIGHT

Compounds with the pyrochlore structure and the formula $A^{III}_2B^{IV}_2O_7$ (where A = rare earth ions and B = Ti, Ru, Ir, Tc, Sn, Hf, Zr, and Pb) have previously been reported by several investigators.[1-12] Hoekstra and Siegel have recently reported the synthesis of $Tl_2Pt_2O_7$.[9] In this paper we describe the synthesis of a new series of pyrochlore compounds with the formula $A_2Ge_2O_7$. These compounds, produced at elevated temperatures and pressures, further illustrate the extension of the stability field of a structure by the use of high pressure.

Experimental Section

The starting materials were high-purity oxides. GeO_2 (Spex Industries) of 99.999% purity was thoroughly mixed with In_2O_3, Tl_2O_3 (Spex Industries, 99.999%), and the rare earth oxides (Lindsay Chemical Division, American Potash and Chemical Corp.) of at least 99.9% purity. These samples were heated at 1100° for 4 hr at a pressure of 65 kbars and rapidly quenched. $In_2Ge_2O_7$ and $Tl_2Ge_2O_7$ were prepared at 1250 and 900°, respectively. The details of the technique have been published previously.[13,14] The products were recovered as highly dense, sintered pellets with a grain size of ~0.05 mm. An attempt to prepare $Sm_2Ge_2O_7$ resulted in an unidentified product; no trace of a pyrochlore phase could be found in the X-ray pattern.

An X-ray diffraction pattern of $In_2Ge_2O_7$ was taken using a Guinier–de Wolff camera with a KCl internal standard. The films were read on a Mann film reader and d values were calculated using $\lambda(Cu\ K\alpha_1) = 1.54051$ Å and $a(KCl) = 6.2931$ Å. A cell dimension of 9.711 ± 1 Å for $In_2Ge_2O_7$ was determined by a least-squares refinement of 10 reflections. X-Ray patterns of other germanates were taken using a Debye–Scherrer camera of 114.6-mm diameter and Cu Kα radiation. Cell dimensions of these compounds were obtained by a least-squares refinement using a Nelson–Riley function. Table I presents the powder diffraction data for the new germanates. Observed intensities are given only for $In_2Ge_2O_7$; intensities for the remaining pyrochlores are similar. Although merely indexing powder patterns does not represent proof of structure type, it should be noted

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