The Neutron and X-ray Crystal Structure of (Na,Li)$_7$Th$_6$F$_{31}$ with More Than One Least-Squares Minimum*

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The compound (Na,Li)$_7$Th$_6$F$_{31}$ crystallizes in space group $P3c1$ with $a_0 = 9.9056 \pm 0.0003$ and $c_0 = 13.2820 \pm 0.0005$ Å at 25°C. The calculated density is 6.045 g.cm^{-3} and $Z = 2$. There are 18 atoms in the asymmetric unit. Two independent Th^{4+} ions and F(1) through F(10) are on the general position $6(d)$; Th(1) is coordinated by 9F$^-$ and Th(2) is coordinated by 10F$^-$. Ion F(11) is on position $2(a)$. The three sodium ions Na(1), Na(2) and Na(3) occupy positions $2(c)$, $2(b)$ and $2(a)$ respectively. The ion Na(3) is surrounded by 12F$^-$ and Na(2) and Na(1) are surrounded by 6F$^-$ at distances less than 3.0 Å. Sodium (1) and Na(2) have five and three more F$^-$ nearest neighbors respectively between 3.0 and 3.5 Å. Lithium(1) is octahedrally coordinated at position $2(a)$. Lithium(2) is at general position $6(d)$ and is surrounded by 7F$^-$ nearest neighbors less than 3.0 Å distant.

There are at least two least-squares minima for each of two sets of data obtained with X-rays and neutrons. The ranges of cation–anion interatomic distances for the originally determined X-ray and neutron minima are respectively: Th(1)–F, 2.23–2.62, 2.28–2.52 Å; Th(2)–F, 2.25–2.63, 2.29–2.57 Å; Na(1)–F, 2.26–3.54, 2.26–3.41 Å; Na(2)–F, 2.25–3.34, 2.30–3.07 Å; Na(3)–F, 2.56–2.96, 2.50–3.00 Å; Li(1)–F, 2.03–2.06, 1.96–2.06 Å; Li(2)–F, 1.77–2.89, 1.92–2.77 Å. Refinement of the X-ray parameters with neutron data, and *vice versa*, did not change the parameters significantly; two very significant minima remained, with differences as large as 30σ.

Introduction

The ternary system NaF–LiF–ThF$_4$ and its intermediate compounds are being investigated as part of the Molten Salt Breeder Reactor Program at the Oak Ridge National Laboratory (Thoma, Insley, Landau, Friedman & Grimes, 1959; Thoma, Insley, Hebert, Friedman & Weaver, 1963). The ternary intermediate compound (Na,Li)$_7$Th$_6$F$_{31}$ was regarded as the terminus of a solid solution join with the high temperature modification of NaThF$_5$ (α-NaThF$_5$, Brunton, Insley, McVay & Thoma, 1965) and was erroneously reported as NaLi$_2$Th$_2$F$_{11}$. Both phases crystallize with the same space group and have similar unit-cell dimensions.

Experimental

We decided to gather both neutron and X-ray diffraction data for the crystal structure determination. The positions of the thorium atoms and most of the fluorine atoms could be determined from the three-dimensional Patterson sections computed from both sets of data. The best positional parameters and temperature factors for the low atomic number atoms would come from the neutron data.

Single crystals of (Na,^{7}Li)$_7$Th$_6$F$_{31}$ (hereafter referred to as NLT) were selected from an ingot of the composition: NaF–20 mole %, ^{7}LiF–40 mole %, ThF$_5$–40

mole % which was grown in a modified Stockbarger-Bridgman gradient furnace (Weaver, Ross, Sturm, Eorgan & Thoma, 1964). The crystals were tumble-ground in an abrasive-lined ball mill until they were roughly cubic with rounded edges. These crystals were etched smooth in warm concentrated aqueous Al(NO$_3$)$_3$ solution and were thermally shocked by repeated immersions alternately in liquid nitrogen and mineral oil at 20°C. The crystals were translucent after this treatment. One of us (DRS) observed a greenish-blue thermochromism in the crystals at 77°K which may be the result of a phase transition at low temperature. Fragments of the same material were submitted for chemical analysis, the results of which are reported in Table 1.

Thirty-three high angle X-ray reflections were used to refine the unit-cell parameters by least-squares analysis; $a_0 = 9.9056 \pm 0.003$ and $c_0 = 13.2820 \pm 0.0005$ Å at 25°C. (λ, Cu $K\alpha_1 = 1.54050$, Cu $K\alpha_2 = 1.54434$ Å). The space group is $P3c1$ and the conditions limiting possible reflections are: $hh0l$, $l = 2n$ present only. Piezoelectric tests on the Mellon Institute Giebe–Scheibe detector were negative but the final structure, from both X-ray and neutron data, is noncentrosymmetrical.

The calculated density is 6.045 g.cm^{-3}, the measured density is 5.94 g.cm^{-3}, $Z = 2$ and the linear absorption, $\mu = 1735.51$ cm^{-1} for Cu $K\alpha$ radiation, and is less than 0.1 for 1.0770 Å neutrons.

Neutron determination

The crystal used for neutron measurements was about 2mm on a side, and weighed 10.4 mg, somewhat small

Table 1. *Results of chemical analyses of* (Na, ^{7}Li)$_7$Th$_6$F$_{31}$ *crystals*

	^{7}Li	Na	Th	F
Mean %	1·16	4·38	66·72	28·22
Standard deviation for individual	0·11	0·55	0·26	0·31
Number of atoms Th=12	6·92	7·95	12	61·99

Table 2. *Positional parameters and temperature factors for* (Na,Li)$_7$Th$_6$F$_{31}$

ATOM		X	Y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Th(1)	NO[h]	0.0782(4)[b]	0.3954(4)	0.0[c]	0.0012(3)	0.0012(3)	0.0006(2)	0.0006(3)	0.0002(2)	-0.0001(2)
	XN	0.0786(2)	0.3954(2)	0.0	0.0035(2)	0.0029(2)	0.0005(1)	0.0016(2)	0.0000(1)	0.0000(1)
	XO	0.0847(2)	0.4094(2)	0.0	0.0044(2)	0.0039(3)	0.0007(1)	0.0024(2)	0.0000(2)	-0.0003(1)
	NX	0.0850(4)	0.4088(4)	0.0	0.0016(4)	0.0013(4)	0.0003(2)	0.0010(3)	-0.0004(2)	-0.0002(2)
Th(2)	NO	0.9148(4)	0.5911(4)	0.2059(2)	0.0008(3)	0.0017(3)	0.0003(2)	0.0007(3)	0.0001(2)	0.0003(2)
	XN	0.9153(2)	0.5906(2)	0.2060(2)	0.0033(3)	0.0035(2)	0.0006(1)	0.0020(1)	0.0002(1)	0.0000(2)
	XO	0.9214(2)	0.6045(2)	0.2061(2)	0.0036(2)	0.0035(2)	0.00035(9)	0.0017(2)	0.0000(1)	0.0002(1)
	NX	0.9220(4)	0.6043(4)	0.2059(2)	0.0011(4)	0.0013(4)	0.0006(2)	0.0005(3)	0.0002(2)	-0.0001(2)
F(1)	NO	0.1370(7)	0.4291(8)	-0.1862(5)	0.0029(7)	0.0038(7)	0.0007(3)	0.0003(6)	-0.0005(4)	-0.0001(4)
	XN	0.144(4)	0.443(4)	-0.192(3)	0.005(2)	d				
	XO	0.139(4)	0.441(4)	-0.181(3)	0.002(1)	d				
	NX	0.1335(9)	0.4435(9)	-0.1803(6)	0.0036(8)	0.0041(8)	0.0008(3)	0.0010(7)	0.0002(4)	0.0006(4)
F(2)	NO	0.8658(8)	0.5552(7)	0.3853(6)	0.0036(7)	0.0030(7)	0.0009(3)	0.0007(6)	-0.0008(4)	-0.0002(4)
	XN	0.869(3)	0.564(3)	0.376(3)	0.003(2)	d				
	XO	0.864(4)	0.563(4)	0.388(3)	0.002(1)	d				
	NX	0.8615(8)	0.5692(8)	0.3916(4)	0.0025(7)	0.0037(8)	0.0007(3)	0.0001(6)	-0.0002(4)	0.0005(4)
F(3)	NO	0.1191(8)	0.3061(8)	-0.3759(6)	0.0031(7)	0.0039(8)	0.0015(4)	0.0020(6)	0.0011(5)	0.0002(4)
	XN	0.114(4)	0.306(3)	-0.374(3)	0.005(2)	d				
	XO	0.129(5)	0.315(4)	-0.374(3)	0.003(2)	d				
	NX	0.1197(9)	0.3088(9)	-0.3770(6)	0.0028(7)	0.0041(9)	0.0016(4)	0.0018(7)	0.0004(5)	-0.0009(5)
F(4)	NO	0.8781	0.6893(8)	0.5827(6)	0.0037(8)	0.0028(7)	0.0012(4)	0.0015(6)	0.0006(4)	-0.0004(4)
	XN	0.874(4)	0.682(4)	0.586(3)	0.005(2)	d				
	XO	0.886(5)	0.690(4)	0.587(3)	0.003(2)	d				
	NX	0.8784(9)	0.6912(9)	0.5811(6)	0.0028(8)	0.0027(8)	0.0015(4)	0.0013(6)	0.0012(5)	0.0003(5)
F(5)	NO	0.3431(6)	0.5103(7)	-0.0444(5)	0.0015(6)	0.0047(7)	0.0022(3)	0.0001(5)	-0.0005(3)	0.0005(4)
	XN	0.340(4)	0.517(4)	-0.053(3)	0.006(2)	d				
	XO	0.357(5)	0.459(5)	-0.062(3)	0.004(2)	d				
	NX	0.3512(8)	0.4488(8)	-0.0555(6)	0.0031(7)	0.007(1)	0.0025(4)	0.0004(7)	-0.0003(4)	-0.0006(5)
F(6)	NO	0.6479(8)	0.5494(7)	0.2615(5)	0.0069(9)	0.0038(7)	0.0021(3)	0.0006(7)	0.0004(4)	0.0003(4)
	XN	0.646(4)	0.541(4)	0.258(3)	0.008(2)	d				
	XO	0.668(4)	0.493(5)	0.249(3)	0.004(2)	d				
	NX	0.6564(7)	0.4906(8)	0.2501(6)	0.0016(6)	0.0054(8)	0.0021(3)	-0.0001(6)	-0.0007(4)	0.0007(4)
F(7)	NO	0.1033(8)	0.1966(7)	-0.0655(6)	0.0059(8)	0.0025(7)	0.0015(3)	0.0031(7)	-0.0001(4)	-0.0006(4)
	XN	0.112(4)	0.202(4)	-0.071(3)	0.005(2)	d				
	XO	0.079(4)	0.196(4)	-0.061(3)	0.0009(9)	d				
	NX	0.0808(8)	0.1893(8)	-0.0588(7)	0.0033(7)	0.0010(7)	0.0024(4)	0.0000(6)	-0.0001(4)	-0.0010(4)
F(8)	NO	0.9191(7)	0.8111(7)	0.2643(5)	0.0014(6)	0.0031(7)	0.0018(3)	0.0005(6)	0.0009(4)	0.0001(4)
	XN	0.918(3)	0.812(3)	0.257(2)	0.002(2)	d				
	XO	0.893(4)	0.803(3)	0.267(3)	0.0003(9)	d				
	NX	0.8985(9)	0.8058(8)	0.2712(6)	0.0053(8)	0.0038(8)	0.001?(3)	0.0039(7)	-0.0006(4)	-0.0010(5)
F(9)	NO	0.1295(8)	0.5851(7)	-0.3531(6)	0.0026(7)	0.0020(7)	0.0017(4)	0.0003(6)	-0.0014(4)	0.0004(4)
	XN	0.125(4)	0.584(4)	-0.364(3)	0.007(2)	d				
	XO	0.117(4)	0.576(4)	-0.347(3)	0.001(1)	d				
	NX	0.117(1)	0.5787(8)	-0.3459(6)	0.0049(9)	0.0014(7)	0.0014(3)	0.0007(6)	-0.0012(5)	0.0004(4)
F(10)	NO	0.8836(8)	0.4214(8)	0.5508(6)	0.0022(7)	0.0033(7)	0.0013(3)	0.0003(6)	-0.0007(4)	0.0008(4)
	XN	0.879(3)	0.421(3)	0.543(3)	0.004(2)	d				
	XO	0.868(5)	0.417(4)	0.555(4)	0.002(1)	d				
	NX	0.8716(9)	0.4153(8)	0.5578(6)	0.0029(8)	0.0035(8)	0.0016(4)	0.0010(7)	-0.0013(5)	0.0005(5)
F(11)	NO	0.66667	0.33333	-0.306(1)	0.0038(7)	f	0.008(1)	f	f	f
	XN	0.66667	0.33333	-0.321(5)	0.008(3)	d				
	XO	0.66667	0.33333	-0.321(8)	0.012(4)	d				
	NX	0.66667	0.33333	-0.309(2)	0.017(3)	f	0.011(3)	f	f	f
Na(1)	NO	0.66667	0.33333	-0.047(2)	0.002(1)	f	0.003(2)	f	f	f
	XN	0.66667	0.33333	-0.045(4)	0.003(2)	d				
	XO	0.66667	0.33333	-0.055(4)	0.001(2)	d				
	NX	0.66667	0.33333	-0.054(2)	0.005(2)	f	0.0005(8)	f	f	f
Na(2)	NO	0.33333	0.66667	0.258(2)	0.005(2)	f	0.0006(8)	f	f	f
	XN	0.33333	0.66667	0.254(4)	0.005(2)	d				
	XO	0.33333	0.66667	0.248(4)	0.001(1)	d				
	NX	0.33333	0.66667	0.251(2)	0.0005(9)	f	0.003(1)	f	f	f
Na(3)	NO	0.0	0.0	0.121(2)	0.006(2)	f	0.002(2)	f	f	f
	XN	0.0	0.0	0.118(3)	0.005(2)	d				
	XO	0.0	0.0	0.084(5)	0.009(3)	d				
	NX	0.0	0.0	0.083(2)	0.006(2)	f	0.005(2)	f	f	f
Li(1)	NO	0.0	0.0	-0.139(3)	0.003(2)	f	0.002(2)	f	f	f
	XN	0.0	0.0	-0.19(2)	0.02(1)	d				
	XO	0.0	0.0	-0.15(2)	0.008(6)	d				
	NX	0.0	0.0	-0.156(3)	0.004(2)	f	0.000(2)	f	f	f
Li(2)	NO	0.233(4)	0.283(3)	-0.188(3)	0.027(6)[g]	0.004(3)	0.014(4)	-0.011(4)	0.012(4)	-0.001(3)
	XN	0.28(2)	0.29(2)	-0.20(2)	0.01(1)	d				
	XO	0.272(9)	0.310(9)	-0.221(8)	0.003(3)	d				
	NX	0.286(8)	0.250(7)	-0.13(2)	0.04(2)[g]	0.019(7)	0.07(2)	-0.030(9)	0.04(2)	-0.04(1)

[a] Coefficients in the Temperature Factor: EXP$-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{13}hl+2\beta_{23}kl+2\beta_{12}hk)$.

[b] Standard Error (in parentheses) Corresponds to Last Significant Digit in Parameter.

[c] Defines Origin Along Z.

[d] X-Ray Temperature Factors for F, Na, and Li are Constrained to be Isotropic.

[f] Only those β_{ij} Adjusted as Independent Variables are Shown. Symmetry Constraints Upon the β_{ij} of all Atoms in Special Positions are: $\beta_{11}=\beta_{22}=2\beta_{12}$ and $\beta_{13}=\beta_{23}=0$. (Levy (1956)).

[g] Temperature factor is not positive-definite.

[h] XO – Original X-ray Parameters and Data.
NO – Original Neutron Parameters and Data.
XN – X-Ray Data, NO Parameters
NX – Neutron Data, XO Parameters.

for the purpose. Petrographic examination, neutron and X-ray Laue photographs, and X-ray precession photographs confirmed that the crystal remained un-fractured after liquid nitrogen immersion.

Approximately 2200 neutron reflections were measured by the step-scanning method, with the Oak Ridge Automatic Three Circle Neutron Diffractometer at the Oak Ridge Research Reactor (Busing, Smith, Peterson & Levy, 1964) and reduced to a set of intensity data and their corresponding standard errors, by the methods and CDC 1604 Å computer programs described by Brown & Levy (1964). The neutron wavelength was 1·0770 Å. Each measurement comprised 51 steps over a 5° 2θ range; each step corresponded to 20,000 monitor counts. A standard reflection (080) was measured after each 50 reflections. We used an unpublished program by C.K.Johnson to form a set of 1394 independent (non-equivalent) intensities, and their standard errors. In this program, the 400 reflection of a standard NaCl crystal served to establish the absolute scale. When combining the standard errors of redundant equivalent reflections, the root mean-square deviation was selected if it was larger than the square root of the sum of the individual variances. A 3% standard error was combined with the statistical standard error to give the total standard error for least-squares weighting.

Positions of two thorium atoms, one lithium atom, and several fluorine atoms were located in a three-dimensional Patterson calculation. The lithium-7 atom, by virtue of its negative coherent scattering length $(-0\cdot21 \times 10^{-12}$ cm) was readily observed, in the presence of stronger scatterers, within 0·01 Å of its final refined position. The scattering length for lithium-7 was determined by Peterson & Smith (1967); for the other atoms, we used values tabulated by Bacon (1962): 0·35, 1·01, and $0\cdot55 \times 10^{-12}$ cm for sodium, thorium, and fluorine, respectively. The scattering lengths were not varied in the least-squares refinement.

X-ray determination

The neutron data crystal was crushed and the fragments were ground in an air-driven race. A sphere 130 μ in diameter was mounted on a computer controlled Picker four-circle single-crystal orienter equipped with a scintillation-counter detector. All of the independent reflections, $h \geq 0, k \geq 0, l \geq 0$, out to $2\theta = 146°$ were measured with Ni-filtered Cu $K\alpha$ radiation by the 2θ scan technique. Additional equivalent reflections, $\bar{h}k\bar{l}$, were measured at high 2θ angles. The 998 reflection data were corrected for Lorentz–polarization factors and for absorption and were reduced to structure factors, F_o. The scattering factors for Na$^+$, Li$^+$, Th^{4+}, and F$^-$ were taken from Cromer & Waber (1965). The scattering factor for Th^{4+} includes the real and imaginary parts of the anomalous dispersion, $\Delta f' = -4$ and $\Delta f'' = -15$ electrons (*International Tables for X-ray Crystallography* 1962). The anomalous dispersion parts of the scattering factors are used by a modified version of the

Busing, Martin & Levy (1962) least-squares program. The value of -15 electrons for $\Delta f''$ is used because the absolute configuration of the crystal was determined by Hamilton's (1965) significance test on the R factor to be such that $\Delta f'' = -15$ electrons gives the best R factor ($R=0\cdot0600$ for $\Delta f''=15$ electrons and $R=0\cdot0596$ for $\Delta f'' = -15$ electrons) for a one-dimensional hypothesis and 760 degrees of freedom at the 0·005 significance level. (See Ueki, Zalkin & Templeton (1966) and Cruickshank & McDonald (1967) for a discussion of errors caused by neglect of anomalous scattering.)

A three-dimensional Patterson synthesis gave the positions of the Th^{4+} ions at general positions 6(d); Th(1), $x=0\cdot09$, $y=0\cdot41$, $z=0\cdot0$ and Th(2), $x=0\cdot91$, $y=0\cdot59$, $z=0\cdot20$ for starting parameters. The positions of most of the other ions were derived from three-dimensional difference syntheses and by inferences from stereoscopic views of models of the structure.

The atomic positions and temperature factors were adjusted by the method of least-squares with *XFLS*, a modification of the Busing, Martin & Levy (1962) program. The quantity $\Sigma w(F_o - F_c)^2$ was minimized and the summation was over all of the reflections. The refinement was based upon $|F_o|$ for the X-ray data and the corresponding weighting factor was the reciprocal of $\sigma^2(F_o)$, where $\sigma(F_o)=\sigma(F_o^2)/2F_o$. The empirical equation,

$$\sigma^2(F_o^2)=[T+B+0\cdot0225(T-B)^2]/[A(\mathrm{Lp})^2],$$

was used to estimate the variance in this case [Lp = Lorentz–polarization, A =absorption correction, T = total and B =background counts (Busing & Levy, 1957)].

Discussion of results

The initial structure models were based upon the assumption that, regardless of the chemical analysis (Table 1) the stoichiometry was probably close to Na$_6$Li$_6$Th$_{12}$F$_{60}$ because of the preliminary results of phase equilibria studies (Thoma, 1966), which placed a compound of that stoichiometry on a join with NaThF$_5$. We also assumed that the space group was $P\bar{3}c1$ because both piezoelectric and pyroelectric tests were negative. Both assumptions proved to be false.

The usual statistical tests of Wilson (1949) and of Howells, Phillips & Rogers (1949) were ambiguous. Pseudo-symmetric pairs F(7,8) and F(9,10) had large isotropic temperature factors with both X-ray and neutron data and the least-square refinement would not converge. When space group $P3c1$ was tested, the thorium ions remained nearly centrosymmetric but there were large departures from centrosymmetry by most of the fluorine ions, particularly F(7), F(8), F(9) and F(10); F(11) has no pseudo-centrosymmetrical equivalent.

The refinement of the atomic parameters was carried out independently by each of the authors to obtain the final results labeled XO and NO in Table 2. D.P. Shoe-

maker suggested that the large disparity between these sets of parameters might be the result of the convergence of the least-square refinements to two different minima.

The results of refining the XO parameters with neutron data and NO parameters with X-ray data are listed in Table 2. These parameters XN and NX respectively confirm that there are at least two minima for each of the two sets of data. Additional least-squares refinements were made on the parameters with the X-ray data by choosing new starting parameters for the Th ions several standard errors away from XO and NO. The least-squares results either converged on the previous minima or diverged and blew up depending upon how far the new parameters were from the original set. If starting parameters are chosen midway between XO and NO, the least-squares refinement does not converge.

The differences between parameters which refine to the two minima (for each of the two data sets) may be as large as 30σ but with the exception of the thermal parameters, F(1) y parameter and Li(2) x and y parameters, the differences between parameters for each set of data within each minimum are 3σ or less. The

differences between the thermal parameters, β_{11} and β_{22}, for the two independent Th ions obtained from refinement to the same minimum of the neutron and X-ray data are as large as the values obtained in the refinement to the two different minima (Table 2).

The best structure seems to be that represented by the parameters NO (Table 2) from the original neutron data. The discrepancy index R for NO is significantly less than that for NX at the 0·005 significance level and some of the interatomic distances from the XO parameters (Table 2) appear to be unreasonable, e.g. Th(1)–F(2) 2·18 Å; F(1)–F(11) 1·72 Å; Li(2)–F(8) 1·77 Å. The NO structure is, therefore, discussed in the rest of the paper.

The final atomic parameters and temperature factors are listed in Table 2. Anisotropic temperature factors were calculated for all of the atoms from the neutron data and for thorium only from X-ray data. The X-ray temperature factors for all of the fluorine, lithium, and sodium ions are isotropic.

We adjusted the occupancy of the Li and Na sites by least squares and they converged to values which did not differ significantly from full, unmixed occupancy.
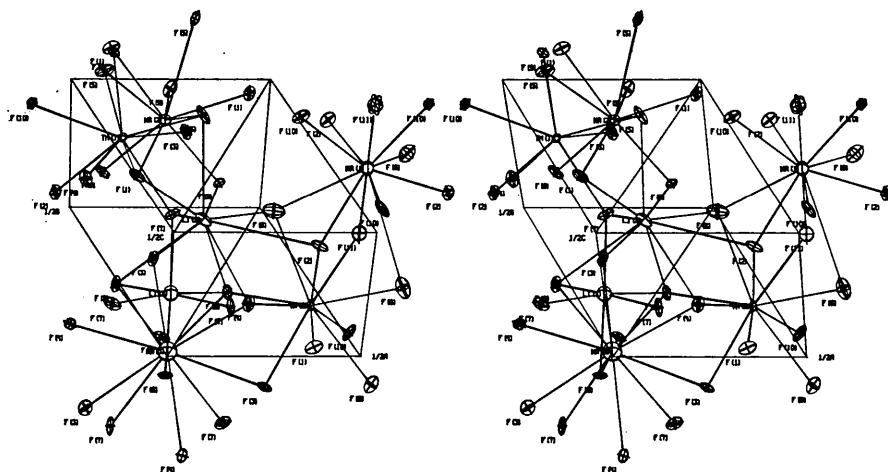
Fig. 1. The cation contents of one asymetrical unit of $(Na,Li)_7Th_6F_{31}$ showing the coordination polyhedron around each cation. One fourth of a unit cell is outlined.
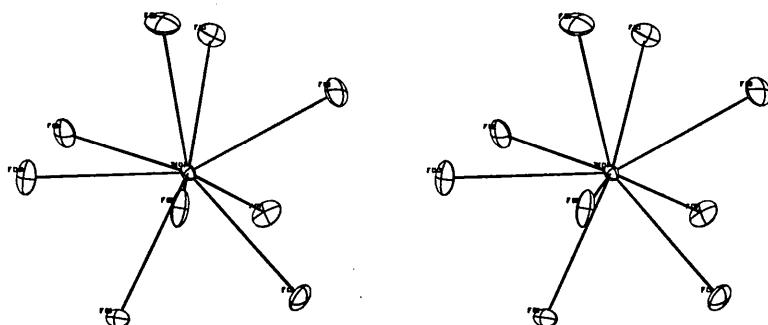
Fig. 2. Coordination polyhedron around Th(1).

The stoichiometry which best fits the crystallographic data is $Na_6Li_8Th_{12}F_{62}$, contrary to the preliminary report (Sears & Brunton, 1967). This result also is in acceptable agreement with the chemical analysis (Table 1). We prefer to use the less specific formula $(Na,Li)_7Th_6F_{31}$ because there is a group of compounds known to have this stoichiometry: $Na_7Zr_6F_{31}$ (Burns, Ellison & Levy, 1968); metastable $Na_7Th_6F_{31}$ and many stable compounds (Thoma, 1962). Furthermore, there appears to be a solid solution join from $(Na,Li)_7Th_6F_{31}$ to α-NaThF$_5$ or a new polymorph of $Na_7Th_6F_{31}$, NLT being the phase limit of LiF solid solution. In fact, this latter possibility provides the most credible explanation for the existing phase equilibrium data in this region of the ternary diagram (Thoma, 1966). We propose that compositions on the low-LiF end of the solid solution join are achieved by simple replacement of lithium in both of its positions by sodium, resulting in a direct way in a composition limit $Na_7Th_6F_{31}$. If, however, the composition limit is $NaThF_5$, it is necessary to construct a more complicated mechanism, e.g. loss of Li(1) from its octahedral position and replacement of lithium by sodium in the general Li(2) position,

accompanied by a loss of fluorine, presumably from the polyhedron surrounding the ten-coordinate thorium, Th(2).

Figs. 1 through 8 are stereoscopic drawings (Johnson, 1965) of the contents of one asymmetrical unit and the coordination polyhedra around Th(1), Th(2), Na(1), Na(2), Na(3), Li(1), and Li(2) respectively. The drawing in Fig. 1 shows the unit cell rotated $-30°$ around a_1 and all of the other Figures are rotated $45°$ around a_1. The choice of the F$^-$ nearest neighbors for Na(1), Na(3) and Li(2) is arbitrary and all of the fluorine ions less than $3·50$ Å distant were included. It should be noted that the four nearest neighbor F$^-$ ions to Li(2) are at the corners of an irregular tetrahedron.

The coordination about Th(1) is the tripyramidal configuration normal for nine-coordinate atoms (Duffey, 1951; Kepert, 1965). The Th(2) environment may also be regarded as derived from the tripyramidal, by the insertion of an additional (fourth) fluorine ion in the central girdle.

The important interatomic distances not corrected for thermal motion are listed in Table 3. In the case of Li(2), corrections for independent thermal motion were
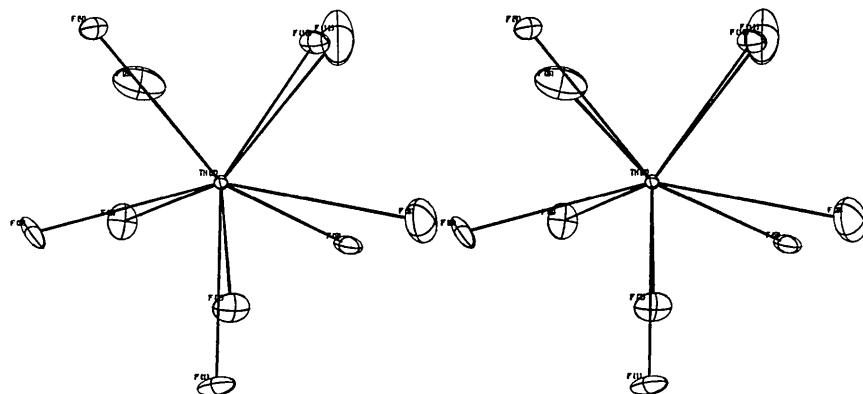
Fig. 3. Coordination polyhedron around Th(2).
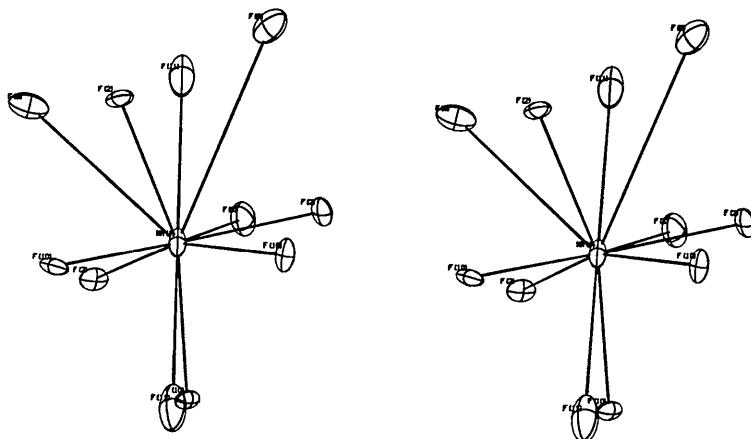
Fig. 4. Coordination polyhedron around Na(1).

calculated; the results corresponded to Li(2)–F bond distances increased by 0·02–0·08 Å, but we are not confident that the large anisotropic thermal motion parameter for Li(2) calculated from the neutron data has any meaning. It is possible that it reflects a positional disorder.

For the most part, interatomic distances appear to be normal. Ligancy corrected Th–F distances are expected to be nearly 2·44 Å for 9- and 10-coordinated thorium (Pauling, 1960), and three thorium–fluorine distances are very significantly shorter than this: Th(1)–F(7), Th(1)–F(4), and Th(2)–F(8). However, the coordination polyhedra about both thorium atoms are quite irregular, and this should relax ligancy effects and packing constraints. The six short Na(1)–F(2) and Na(1)–F(10) distances correspond to an octahedral configuration about the sodium ion, for which an Na–F distance of 2·31 Å is expected (Pauling, 1960). There are no unusual F–F distances.

The observed X-ray structure factors and calculated structure factors from the XO parameters are listed in Table 4. The discrepancy index $R = \Sigma \left| |F_o| - |F_c| \right| / \Sigma |F_o|$ is 0·0596 for all X-ray reflections and the standard deviation of an observation of unit weight, $[\Sigma w (F_o - F_c)^2 / (n_o - n_v)]^{1/2}$ is 0·80 (n_o is the number of reflections and

n_o the number of variables). The discrepancy index for XN (Table 2) is 0·0598.

Table 3. *Interatomic distances for* (Na,Li)₇Th₆F₃₁ *determined form the* XO *and* NO *parameters* (*Table* 2)

The number in parentheses is the standard error corresponding to the last digit.

|	XO	NO		XO	NO		XO	NO
Th(1)–F(7)	2.23(3)A	2.277(6)A	Th(2)–F(6)	2.25(4)A	2.425(6)A	Li(2)–F(8)	1.77(9)	1.92(3)
–F(9)	2.34(4)	2.351(6)	–F(8)	2.26(3)	2.293(6)	–F(6)	2.27(9)	2.03(3)
–F(4)	2.35(4)	2.297(6)	–F(3)	2.32(4)	2.378(6)	–F(1)	2.33(9)	2.08(4)
–F(3)	2.38(4)	2.371(6)	–F(4)	2.36(4)	2.383(6)	–F(5)	2.47(9)	2.75(3)
–F(5)	2.38(4)	2.352(5)	–F(1)	2.40(4)	2.386(6)	–F(3)	2.49(9)	2.77(4)
–F(2)	2.41(4)	2.380(6)	–F(10)	2.41(4)	2.355(6)	–F(9)	2.62(9)	3.18(3)
–F(1)	2.45(4)	2.522(6)	–F(9)	2.43(3)	2.510(6)	–F(7)	2.70(9)	1.98(3)
–F(10)	2.49(4)	2.435(6)	–F(6)	2.44(4)	2.573(6)	–F(4)	2.89(9)	3.37(3)
–F(5)	2.63(4)	2.354(6)	–F(2)	2.46(4)	2.425(6)			
			–F(11)	2.63(2)	2.514(3)			
Na(1)–3F(10)	2.26(5)	2.26(2)	Na(2)–3F(9)	2.25(4)	2.30(2)	Na(3)–3F(7)	2.56(6)	3.00(2)
–3F(2)	2.27(4)	2.29(1)	–3F(1)	2.30(4)	2.299(8)	–3F(4)	2.69(4)	2.730(6)
–3F(6)	3.04(6)	3.41(2)	–3F(5)	3.34(6)	3.07(2)	–3F(3)	2.78(4)	2.649(6)
–F(11)	3.1(2)	3.18(3)	Li(1)–3F(8)	2.0(1)	2.06(3)	–3F(8)	2.96(6)	2.50(2)
–F(11)	3.5(2)	3.46(3)	–3F(7)	2.1(1)	1.96(2)			
F(1)–F(2)	2.53(4)	2.51T(5)	F(1)–F(9)	2.64(6)	2.717(8)	F(1)–F(5)	2.72(6)	2.838(8)
F(1)–F(7)	2.72(6)	2.688(7)	F(1)–F(5)	2.62(6)	2.593(7)	F(1)–F(3)	2.83(6)	2.763(8)
F(2)–F(4)	2.90(5)	2.915(8)	F(2)–F(7)	2.88(5)	3.141(8)	F(2)–F(8)	2.76(5)	2.817(8)
F(2)–F(10)	2.66(6)	2.623(8)	F(2)–F(6)	2.51(5)	2.696(8)	F(2)–F(6)	2.80(5)	2.761(8)
F(3)–F(4)	2.65(6)	2.718(9)	F(3)–F(7)	2.72(6)	2.702(8)	F(3)–F(5)	2.96(6)	2.893(8)
F(3)–F(9)	2.67(5)	2.713(8)	F(3)–F(4)	2.86(7)	2.724(9)	F(3)–F(9)	2.67(6)	2.724(8)
F(3)–F(8)	2.94(5)	2.714(8)	F(4)–F(7)	2.74(5)	2.942(8)	F(4)–F(10)	2.77(5)	2.723(8)
F(4)–F(10)	2.66(6)	2.712(8)	F(4)–F(8)	2.59(6)	2.669(8)	F(4)–F(6)	2.76(6)	2.812(8)
F(5)–F(10)	2.64(6)	2.794(8)	F(5)–F(7)	2.68(5)	2.828(7)	F(5)–F(7)	3.05(5)	2.726(8)
F(6)–F(11)	1.82(7)	2.416(8)	F(6)–F(10)	2.78(6)	3.041(8)	F(6)–F(6)	2.71(7)	3.88(2)
F(6)–F(6)	2.71(7)	3.88(2)	F(6)–F(9)	2.89(6)	2.593(9)	F(6)–F(6)	2.76(5)	2.638(7)
F(7)–F(8)	2.80(4)	2.757(6)	F(7)–F(7)	2.94(5)	2.921(9)	F(7)–F(7)	2.94(5)	2.921(9)
F(7)–F(8)	2.91(4)	2.849(6)	F(8)–F(8)	2.93(5)	2.816(9)	F(8)–F(8)	2.93(5)	2.816(9)
F(9)–F(10)	2.53(4)	2.503(5)	F(10)–F(11)	2.26(5)	2.26(2)	F(10)–F(10)	3.00(7)	3.24(2)
F(10)–F(10)	3.00(7)	3.24(2)						
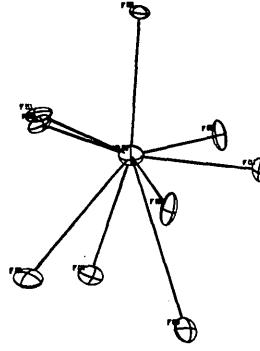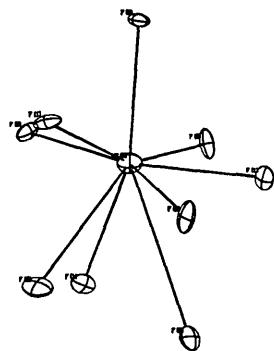
Fig. 5. Coordination polyhedron around Na(2).
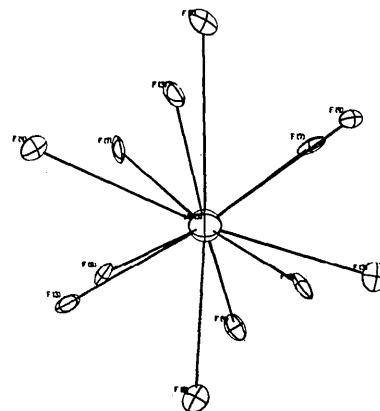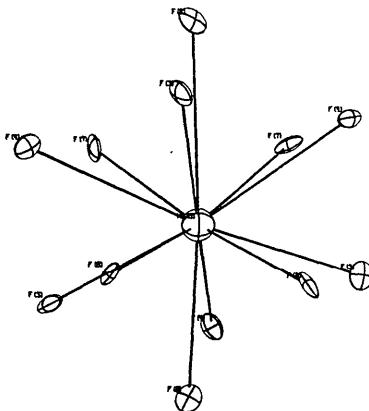
Fig. 6. Coordination polyhedron around Na(3).

The final neutron structure factors appear in Table 5, in which $|FOBS|^2 = 10^{24} |F_o|^2$ cm². These data correspond to the NO parameters listed in Table 2 and yield for all data:

$$R_1 = \Sigma \, ||F_o| - |F_c||/\Sigma|F_o| = 0.096$$

and

$$R_2 = \Sigma \, ||F_o|^2 - |F_c|^2|/\Sigma \, |F_o|^2 = 0.110 \, .$$

Table 4. *The observed and calculated structure factors and α angles for X-ray data*

$$\alpha \times 10$$

Table 4 (cont.)

Actual least-squares adjustments, however, minimized the function $\Sigma w||F_o|^2 - |F_c|^2|^2$, in which the weights, w, were taken as $1/\sigma^2$ (F_o) if $|F_o|^2 \geq 2\sigma$, and zero if $|F_o|^2 < 2\sigma$. For the data greater than 2σ, the R values defined above become: $R_1 = 0.061$, $R_2 = 0.091$. The standard deviation of an observation of unit weight,

$$\sigma = [\Sigma w(|F_o|^2 - |F_c|^2)^2/(n_{obs} - n_{var})]^{1/2} \, ,$$

is 1.25 for the data greater then 2σ, and 1.17 for all data. The discrepancy indices R_1 and R_2 for NX (Table 2) are respectively 0.1096 and 0.1279.

We owe a great debt to C. K. Johnson for supervising the data collection on the Oak Ridge Automatic Three Circle Neutron Diffractometer, and for introducing one of us (DRS) to neutron diffraction methods. We

Fig. 7. Coordination polyhedron around Li(1).

thank H. A. Friedman for supplying the lithium-7 material. J. C. Ogle and H. G. Smith graciously provided X-ray and neutron Laue equipment. L. E. Alexander made available to us the Mellon Institute piezoelectric detector. We appreciate the time D. P. Shoemaker spent in reviewing the original draft.

Table 5. *The square of the observed and calculated structure factors and the α angles for neutron data*

$|FOBS|^2 = 10^{23}|F_o|^2(cm)^2$.

The tabulated values have been multiplied by 10.

L	FOBS	FCAL	ALPHA
0 0 L			
2	57	59	77
4	87	86	1706
6	56	53	125
8	21	22	628
10	25	27	51
12	28	31	1139
14	71	72	1779
16	185	195	1655
18	129	130	31
20	97	98	273
0 1 L			
0	24	25	1715
2	23	26	1780
4	16	17	128
6	155	163	18
8	26	22	205
10	49	49	443
12	19	18	156
14	41	42	1613
16	31	32	622
18	22	24	1130
0 2 L			
0	3	8	103
2	44	45	1792
4	5	9	883
6	65	62	197
8	31	30	1440
10	52	45	0
12	18	16	1291
14	20	24	1264
16	99	97	119
18	80	82	240
0 3 L			
0	21	18	1566
2	16	13	1339
4	65	61	24
6	18	19	1587
8	54	54	112
10	130	131	58
12	34	37	128
14	84	85	1706
16	31	30	1763
18	18	16	920
0 4 L			
0	160	173	1664
2	159	165	1713
4	49	48	1558
6	52	50	232
8	49	46	1771
10	20	20	1061
12	132	135	1704
14	33	29	1624
16	176	185	85
18	13	19	983
0 5 L			
0	108	107	1672
2	29	30	141
4	64	62	131
6	65	61	1518
8	30	26	113
10	53	49	1583
12	13	20	1274
14	22	23	1411
16	17	21	639
18	22	33	1354
0 6 L			
0	29	30	983
2	40	41	521
4	16	20	749
6	41	41	1314
8	31	30	402
10	56	54	1628
12	70	71	351
14	119	123	77
16	46	46	1071
0 7 L			
0	32	36	611
2	21	25	921
4	28	26	606
6	14	12	957
8	58	57	16
10	57	56	1455
12	163	165	1732
14	45	46	166
16	27	31	1322
0 8 L			
0	105	105	1620
2	119	114	78
4	40	37	204
6	35	37	1473
8	90	92	1721
10	26	33	1710
12	58	55	166
14	82	79	180
0 9 L			
0	98	96	8
2	59	61	461
4	29	29	71
6	57	57	453
8	54	57	1792
10	19	17	1119
12	54	53	484
14	11	10	62
0 10 L			
0	92	91	113
2	65	69	228
4	25	27	1763
6	16	20	18
8	45	48	58
10	75	74	278
12	9	26	275
0 11 L			
0	31	33	1538
2	40	45	177
4	13	25	723
6	77	73	23
8	78	75	1642
10	42	37	1692
0 12 L			
0	64	62	14
2	27	28	923
4	67	68	1764
6	32	36	1613
1 0 L			
2	29	31	21
4	3	6	314
6	41	39	1640
8	26	25	1560
10	37	34	1780
12	87	85	92
14	21	18	292
16	16	20	1689
18	13	20	104[illegible]
1 1 L			
0	30	29	1800
1	63	66	1772
2	18	18	1684
3	44	44	1792
4	18	18	1119
5	35	33	1792
6	46	41	209
7	86	85	20
8	30	29	1463
9	47	50	146
10	67	63	1736
11	117	116	1677
12	11	15	590
13	60	59	1566
14	40	40	280
15	18	19	1358
16	26	21	14
17	77	69	125
18	16	17	1735
19	21	2	952
1 2 L			
0	7	12	21
1	21	19	1648
2	10	10	1020
3	30	30	1481
4	15	14	492
5	126	127	103
6	90	90	1782
7	49	47	1674
8	28	27	332
9	77	78	1547
10	82	78	157
11	26	22	1554
12	17	15	14
13	74	72	251
14	57	57	167
15	51	51	21
16	12	4	518
17	75	73	1655
18	14	22	520
19	27	33	1587
1 3 L			
0	20	21	929
1	48	44	208
2	66	66	138
3	64	62	142
4	116	111	146
5	69	63	0
6	26	24	1648
7	18	14	1137
8	107	108	1766
9	26	20	1724
10	21	23	1468
11	35	41	376
12	15	12	1041
13	16	19	1528
14	20	23	1749
15	25	29	125
16	13	12	816
17	9	13	1674
18	44	43	1769
19	10	21	1229
1 4 L			
0	81	80	102
1	24	24	83
2	59	58	1518
3	6	6	876
4	31	32	1759
5	10	11	1635
6	13	10	809
7	74	74	206
8	25	27	1666
9	38	35	0
10	43	38	75
11	67	68	14
12	36	35	1574
13	13	17	883
14	28	25	1461
15	18	5	133
16	43	41	1618
17	26	20	227
18	29	30	87
1 5 L			
0	23	23	213
1	76	69	1749
2	93	89	27
3	63	64	37
4	21	15	303
5	59	59	101
6	21	26	1451
7	51	49	1590
8	16	15	1715
9	82	81	1777
10	51	50	523
11	21	26	1743
12	32	32	8
13	100	101	123
14	16	16	1761
15	75	71	188
16	34	32	1756
17	17	19	81
18	21	17	951
1 6 L			
0	20	30	1361
1	8	11	326
2	77	68	73
3	25	22	61
4	35	35	803
5	71	70	1675
6	63	62	66
7	61	60	1386
8	67	67	285
9	31	30	65
10	37	36	183
11	75	76	237
12	33	35	1789
13	24	18	1792
14	23	15	1474
15	29	31	1592
16	10	6	748
17	36	34	1475
1 7 L			
0	13	12	96
1	28	25	156
2	17	18	16
3	23	27	1763
4	97	90	1738
5	121	121	1616
6	61	64	1704
7	63	59	1770
8	69	70	146
9	10	19	1510
10	6	6	1120
11	25	18	1621
12	17	16	1758
13	31	26	742
14	19	26	1734
15	42	37	1683
16	5	25	1601
1 8 L			
0	82	77	1496
1	36	38	1743
2	13	14	1405
3	22	19	367
4	10	16	948
5	48	46	152
6	25	19	191
7	14	21	468
8	26	26	427
9	22	19	1625
10	19	18	241
11	81	83	1750
12	21	11	1295
13	27	27	1712
14	15	15	236
15	37	42	1406
1 9 L			
0	45	43	196
1	96	96	56
2	80	78	1725
3	20	20	938
4	17	21	1169
5	41	47	1489
6	38	42	448
7	79	74	1728
8	41	45	304
9	62	62	253
10	24	9	1080
11	71	76	24
12	21	6	1626
13	12	12	202
1 10 L			
0	45	43	20
1	86	80	223
2	18	19	1201
3	5	17	1066
4	26	26	1379
5	26	28	710
6	38	32	424
7	80	86	249
8	45	41	1695
9	41	36	393
10	45	45	1655
11	19	15	1634
1 11 L			
0	29	24	1371
1	61	61	1670
2	49	52	1503
3	74	75	1800
4	23	6	26
5	30	25	148
6	43	45	231
7	74	74	212
8	4	14	998
9	31	32	97
1 12 L			
0	24	24	1114
1	13	25	255
2	51	52	153
3	40	44	282
4	32	31	180
5	29	17	1362
2 0 L			
2	59	58	134
4	44	42	1504
6	107	101	1639
8	44	41	1792
10	101	99	1767
12	32	26	1715
14	14	17	1621
16	81	79	1654
18	11	16	1443
2 1 L			
0	12	12	21
1	32	30	28
2	18	17	1581
3	32	31	156
4	6	5	414
5	108	108	1740
6	40	40	300
7	74	71	1618
8	14	14	226
9	0	13	1779
10	43	36	34
11	106	105	140
12	79	74	1786
13	65	61	1716
14	33	36	1482
15	66	69	1538
16	47	46	1625
17	7	7	435
18	27	29	948
19	29	28	209
2 2 L			
0	35	34	1800
1	26	25	616
2	72	71	123
3	69	67	194
4	79	73	79
5	34	33	1477
6	43	39	69
7	23	23	834
8	18	18	168
9	35	32	31
10	7	10	1036
11	30	35	1704
12	7	6	589
13	11	20	187
14	17	18	554
15	25	23	1740
16	23	23	284
17	22	14	1024
18	60	61	1645
19	27	32	1746
2 3 L			
0	28	28	452
1	29	31	748
2	71	67	95
3	56	53	1724
4	33	32	105
5	68	67	1532
6	11	6	486
7	43	44	231
8	18	15	455
9	88	85	29
10	34	30	121
11	36	31	1024
12	37	36	117
13	47	41	1559
14	23	17	1611
15	46	51	1471
16	48	47	1650
17	50	55	241
18	51	51	1615
2 4 L			
0	40	40	128
1	49	46	97
2	93	90	1709
3	2	4	432
4	42	37	1736
5	33	31	132
6	28	29	911
7	22	19	1632
8	8	5	207
9	42	42	186
10	78	76	182
11	24	16	1607
12	49	39	99
13	28	27	1336
14	14	15	854
15	25	24	1587
16	26	1	1436
17	38	43	1636
18	90	91	273
2 5 L			
0	9	10	515
1	100	99	1649
2	30	29	47
3	78	77	1681
4	53	49	1611
5	19	14	1488
6	86	81	140
7	81	83	202
8	10	9	26
9	39	38	282
10	34	34	1739
11	48	49	1674
12	14	14	53
13	28	27	829
14	47	48	166
15	60	59	97
16	44	41	246
17	70	66	251
2 6 L			
0	22	20	866
1	66	59	186
2	51	52	221
3	51	45	1593
4	9	12	1719
5	29	20	114
6	52	49	1592
7	14	13	1252
8	16	17	992
9	7	12	419
10	0	21	1497
11	30	31	905
12	21	23	242
13	48	51	1714
14	21	17	73
15	10	14	1347
16	20	30	1713
2 7 L			
0	18	19	75
1	88	86	1770
2	33	31	1294
3	25	13	1376
4	9	10	752
5	56	49	126
6	58	55	1784
7	27	28	31
8	17	17	1333
9	44	44	1516
10	34	39	368
11	31	33	1500
12	29	29	1669
13	26	29	507
14	31	43	1742
15	69	69	280
2 8 L			
0	29	21	1281
1	32	34	466
2	27	32	1702
3	25	14	1515
4	32	35	0
5	30	29	1698
6	58	62	70
7	44	41	325
8	10	5	1295
9	54	55	1615
10	21	19	152
11	48	47	1238
12	43	43	1546
13	60	63	1440
14	26	22	605
2 9 L			
0	8	14	1442
1	8	23	1254
2	29	27	21
3	69	69	30
4	12	24	708
5	43	45	69
6	14	5	1364
7	29	24	485
8	25	30	1608
9	34	28	1727
10	25	31	1476
11	22	17	74
12	27	21	306
2 10 L			
0	6	12	515
1	48	47	1326
2	24	19	1589
3	5	12	192
4	27	32	1697
5	7	13	363
6	23	20	1603
7	10	17	1278
8	21	11	1709
9	44	48	1639
10	31	8	1206
2 11 L			
0	11	14	1660
1	44	44	27
2	22	15	1415
3	20	26	20
4	16	17	1715
5	7	19	617
6	37	42	291
3 0 L			
2	39	40	350
4	174	191	1773
6	101	98	1789
8	44	41	297
10	42	40	44
12	16	9	713
14	31	28	72
16	16	7	1187
18	18	6	595
3 1 L			
0	19	21	929
1	22	22	474
2	86	82	98
3	72	69	1800
4	4	5	1579
5	9	11	1672
6	40	39	358
7	7	6	1046
8	86	83	102
9	13	11	1269
10	58	54	1800
11	45	41	26
12	95	93	1773
13	19	19	409
14	18	21	219
15	14	21	636
16	39	42	135
17	36	30	1638
18	19	12	1024
19	37	40	313
3 2 L			
0	29	28	452
1	129	131	1730
2	44	42	1565
3	41	42	1624
4	38	36	1406
5	61	59	173
6	66	65	155
7	29	29	196
8	37	34	64
9	52	49	1642
10	4	16	551
11	77	76	1559
12	20	6	518
13	26	27	170
14	13	13	1628
15	50	47	294
16	24	14	49
17	73	72	106
18	34	36	368
3 3 L			
0	34	35	0
1	53	51	79
2	30	26	23
3	28	28	641
4	4	10	1488
5	20	19	727
6	45	35	167
7	107	101	1792
8	73	72	1718
9	78	77	1540
10	87	89	1736
11	62	58	75
12	21	12	284
13	34	36	1401
14	32	27	1647
15	22	22	1413
16	24	30	865
17	79	85	1588
18	20	27	71
3 4 L			
0	22	21	1732
1	18	15	567
2	68	69	1769
3	51	50	43
4	22	9	1209
5	58	51	1690
6	128	118	23
7	47	46	1703
8	85	79	81
9	23	31	1618
10	62	61	1730
11	13	13	1212
12	12	13	125
13	25	31	1105
14	16	26	758
15	20	21	1762
16	14	20	592
17	18	22	1390
3 5 L			
0	28	35	494
1	25	24	470
2	14	8	924
3	37	36	235
4	76	73	214
5	27	29	842
6	8	5	371
7	92	92	88
8	67	65	1601
9	27	32	255
10	28	27	1750
11	22	13	1782
12	19	14	47
13	35	39	1444
14	30	21	190
15	21	9	1352
16	28	39	1728
3 6 L			
0	38	38	1622
1	54	55	127
2	29	31	856
3	111	106	47
4	78	73	49
5	59	58	156
6	29	31	106
7	69	68	1730
8	41	40	1786
9	25	25	276
10	0	7	73
11	46	45	369
12	20	22	1548
13	89	87	79
14	37	34	422
15	18	8	759
3 7 L			
0	32	31	1635
1	19	19	116
2	19	19	1273
3	3	20	1623
4	17	10	1041
5	45	45	1773
6	34	29	1707
7	44	48	342
8	13	5	1155
9	52	47	197
10	69	69	8
11	43	42	713
12	19	13	555
13	18	16	1786
14	4	17	472
3 8 L			
0	12	17	1699
1	30	26	1487
2	24	28	29
3	76	79	1612
4	95	96	81
5	34	40	1173
6	11	7	696
7	9	13	620
8	90	86	1782
9	41	43	215
10	52	50	95
11	33	35	418
12	54	59	193
3 9 L			
0	5	14	808
1	32	30	1628
2	33	40	571
3	31	23	175
4	66	63	1703
5	25	17	11
6	39	34	1497
7	28	28	1488
8	15	17	1627
9	38	36	1688
10	16	12	798

Table 5 (*cont.*)

L	FOBS	FCAL	ALPHA
3 10 L			
0	21	21	282
1	50	54	222
2	72	68	81
3	78	84	1720
4	72	75	1634
5	69	64	1592
6	70	74	1648
7	28	13	1223
8	23	28	374
3 11 L			
0	13	6	1349
1	8	23	1648
2	21	34	31
3	31	42	1061
4 0 L			
2	155	161	37
4	137	140	157
6	37	38	1684
8	40	37	229
10	37	36	1417
12	118	113	124
14	127	131	117
16	56	51	1553
18	110	111	1753
4 1 L			
0	80	80	102
1	8	8	597
2	21	25	993
3	12	12	1131
4	43	40	1786
5	39	38	0
6	38	34	1643
7	29	26	1433
8	34	29	0
9	28	24	327
10	26	20	97
11	3	11	1749
12	22	14	720
13	19	15	939
14	57	56	257
15	64	63	211
16	53	50	1540
17	26	21	11
18	43	48	85
4 2 L			
0	41	40	128
1	8	3	1353
2	16	5	1784
3	42	41	213
4	52	51	1746
5	16	8	904
6	20	21	1589
7	66	64	74
8	16	8	84
9	36	31	1631
10	50	52	269
11	4	1	395
12	23	17	1199
13	20	17	1303
14	30	30	1521
15	6	3	93
16	78	81	1744
17	13	10	1079
18	12	9	1358
4 3 L			
0	22	21	1732
1	9	3	524
2	39	38	1751
3	33	27	1729
4	44	40	1636
5	39	36	1515
6	54	51	39
7	47	44	1780
8	144	144	1747
9	29	30	1676
10	57	51	1738
11	30	31	1726
12	94	92	84
13	29	32	198
14	48	47	55
15	28	20	1224
16	14	11	751
17	38	38	1582
4 4 L			
0	168	177	0
1	29	19	1800
2	62	60	543
3	19	18	465
4	101	101	1792
5	40	38	236
6	24	25	1250
7	25	30	783
8	38	39	473
9	20	14	1538
10	69	65	124
11	3	12	1362
12	41	36	24
13	20	12	647
14	103	106	1786
15	34	35	1632
16	105	101	1612
4 5 L			
0	40	37	817
1	39	38	318
2	38	36	908
3	10	13	237
4	62	60	1508
5	10	16	804
6	25	25	1159
7	23	15	646
8	17	17	1091
9	29	29	209
10	31	29	433
11	69	65	33
12	28	33	1467
13	25	10	113
14	31	32	1576
15	31	26	44
4 6 L			
0	44	44	1461
1	19	22	648
2	51	45	1480
3	41	39	316
4	53	48	68
5	13	8	1671
6	37	33	62
7	24	23	1618
8	21	16	1306
9	19	18	1630
10	38	36	1701
11	21	16	1461
12	69	68	1717
13	28	21	61
14	55	50	1769
4 7 L			
0	47	48	85
1	30	26	1800
2	41	39	357
3	44	48	1575
4	29	26	135
5	23	23	1601
6	63	60	1612
7	21	18	1433
8	35	31	54
9	40	44	243
10	93	88	0
11	37	40	158
12	39	47	222
13	21	12	1722
4 8 L			
0	31	27	989
1	32	33	160
2	62	59	1644
3	25	23	1335
4	63	61	225
5	17	14	1588
6	81	79	34
7	29	22	1786
8	57	61	230
9	18	18	1251
10	29	29	1615
11	16	20	1432
4 9 L			
0	62	63	1416
1	28	19	566
2	32	28	1722
3	16	9	200
4	34	30	537
5	13	5	1031
6	56	59	336
7	43	39	0
8	49	47	286
9	0	11	1721
4 10 L			
0	52	48	1630
1	39	40	1126
2	52	54	142
3	17	22	1546
4	15	19	230
5	19	14	1625
5 0 L			
2	5	2	954
4	6	14	1287
6	38	37	8
8	42	42	1757
10	55	50	558
12	0	10	1645
14	30	27	209
16	75	77	21
18	40	47	1588
5 1 L			
0	25	23	213
1	58	58	97
2	10	1	588
3	36	34	44
4	37	35	1334
5	48	49	1800
6	48	44	1600
7	20	9	1746
8	18	17	891
9	88	90	92
10	7	7	578
11	118	119	76
12	57	58	1604
13	48	44	49
14	69	73	1784
15	75	73	1653
16	40	36	180
17	17	16	1358
18	34	43	92
5 2 L			
0	14	10	515
1	11	9	623
2	5	8	810
3	55	55	1613
4	50	44	164
5	36	33	1152
6	25	27	440
7	60	59	133
8	38	39	1589
9	57	55	565
10	72	66	1792
11	48	46	1580
12	22	27	166
13	39	42	1465
14	13	18	1610
15	15	8	522
16	16	24	1533
17	76	75	155
5 3 L			
0	33	35	494
1	71	71	1621
2	3	7	1112
3	68	64	1573
4	28	27	674
5	20	19	27
6	66	64	18
7	35	33	1022
8	27	30	212
9	58	53	35
10	11	11	811
11	38	33	1345
12	49	44	1712
13	13	13	1600
14	30	34	84
15	22	32	673
16	24	26	404
5 4 L			
0	36	37	817
1	45	42	128
2	77	78	128
3	42	40	1447
4	38	37	320
5	31	35	1695
6	34	28	872
7	36	32	1625
8	37	41	105
9	33	37	1481
10	10	5	849
11	7	5	1175
12	41	40	8
13	8	20	513
14	15	19	1366
15	53	57	0
5 5 L			
0	57	54	1800
1	39	40	1695
2	48	46	1691
3	73	69	1714
4	27	22	230
5	38	42	21
6	21	22	299
7	77	75	73
8	10	12	1333
9	17	21	747
10	31	30	1342
11	61	60	1763
12	23	12	1358
13	107	110	1717
14	65	71	203
5 6 L			
0	27	19	1568
1	71	74	1731
2	24	23	1547
3	27	27	914
4	26	29	884
5	27	22	736
6	58	56	1596
7	26	25	1568
8	25	22	1165
9	98	94	1596
10	50	56	286
11	51	51	1348
12	25	34	1548
13	27	22	598
5 7 L			
0	30	25	1648
1	18	10	412
2	56	53	101
3	79	83	175
4	18	10	549
5	85	84	165
6	18	21	624
7	35	33	774
8	77	76	1630
9	41	43	1564
10	34	36	44
11	31	28	1121
5 8 L			
0	64	62	118
1	9	12	1651
2	41	36	1264
3	19	15	748
4	43	41	1608
5	25	16	1773
6	31	24	85
7	34	33	266
8	3	20	398
9	52	49	138
5 9 L			
0	31	22	500
1	22	18	1518
2	76	81	47
3	92	87	102
4	19	13	1676
5	38	43	226
6	30	29	1661
6 0 L			
2	15	20	1625
4	40	43	491
6	127	124	102
8	37	38	61
10	31	31	854
12	68	66	1761
14	14	10	1079
16	17	14	147
6 1 L			
0	30	30	1361
1	76	73	41
2	30	32	1172
3	81	75	95
4	44	44	161
6	62	61	1486
7	23	23	1007
8	18	26	1519
9	56	53	1691
10	33	36	314
11	32	32	882
12	47	47	99
13	53	51	325
14	23	16	1079
15	20	18	824
16	13	2	550
17	65	70	1631
6 2 L			
0	21	20	866
1	14	21	1690
2	8	8	1382
3	31	29	1457
4	21	20	259
5	38	34	290
6	69	67	184
7	60	56	187
8	30	28	340
9	29	26	1239
10	19	27	107
11	14	17	209
12	22	22	1800
13	26	33	1800
14	27	32	1587
15	43	40	271
16	34	27	261
6 3 L			
0	44	38	1622
1	21	16	121
2	51	48	1577
3	58	61	146
4	11	10	288
5	50	50	1630
6	31	30	380
7	34	31	1786
8	31	34	78
9	44	42	1757
10	20	21	1776
11	84	80	30
12	20	9	473
13	91	86	144
14	95	96	162
15	39	35	1792
6 4 L			
0	43	49	1461
1	61	59	1659
2	122	116	81
3	37	33	162
4	24	23	290
5	13	9	891
6	31	33	1780
7	21	21	1503
8	29	26	1746
9	26	20	128
10	38	32	1752
11	22	16	311
12	16	14	777
13	44	43	0
14	44	50	360
6 5 L			
0	19	19	1568
1	35	35	259
2	13	6	987
3	44	43	1607
4	21	19	1008
5	74	72	1545
6	39	39	1620
7	74	73	1753
8	18	13	108
9	48	48	353
10	48	49	178
11	8	4	197
12	44	40	1471
13	59	56	1764
6 6 L			
0	11	5	0
1	21	18	314
2	23	27	785
3	28	26	68
4	25	27	1446
5	29	23	1050
6	35	33	324
7	31	38	1716
8	34	36	1187
9	31	22	1563
10	62	61	1776
11	27	29	499
6 7 L			
0	12	11	983
1	30	35	61
2	29	34	322
3	38	37	1768
4	21	25	119
5	9	2	1709
6	32	38	633
7	16	22	64
8	67	68	1749
9	68	69	111
6 8 L			
0	49	52	207
1	70	71	442
2	12	14	539
3	22	11	1177
4	45	49	1676
5	29	26	1273
6	39	35	1757
7 0 L			
2	48	49	116
4	182	190	36
6	54	56	1557
8	121	117	1777
10	80	78	94
12	50	45	1641
14	5	17	442
16	0	18	1275
7 1 L			
0	22	12	96
1	25	24	1774
2	28	30	138
3	48	43	506
4	50	47	1724
5	26	20	1228
6	17	19	1663
7	27	30	1647
8	8	8	335
9	43	38	1757
10	91	89	112
11	52	50	1789
12	33	38	320
13	33	34	177
14	27	27	1616
15	20	12	67
16	14	11	576
7 2 L			
0	27	19	75
1	93	90	174
2	82	76	0
3	64	61	1588
4	40	40	1622
5	77	77	1722
6	64	63	1784
7	19	26	1139
8	12	16	500
9	34	32	486
10	26	22	62
11	20	22	1376
12	40	39	1749
13	54	54	1704
14	19	23	1555
15	51	54	1549
7 3 L			
0	32	31	1635
1	16	16	1789
2	24	20	569
3	33	33	98
4	16	13	1699
5	80	82	146
6	0	11	491
7	46	45	108
8	60	59	96
9	44	44	852
10	16	12	1149
11	32	28	1356
12	19	24	1406
13	43	38	258
14	8	11	497
7 4 L			
0	48	48	85
1	30	28	180
2	81	80	16
3	31	35	460
4	114	113	1761
5	47	45	195
6	39	30	1572
7	23	23	16
8	44	42	0
9	27	21	1534
10	32	30	186
11	12	12	1430
12	33	28	1503
13	7	29	1093
7 5 L			
0	24	25	1648
1	39	41	207
2	30	20	1734
3	17	6	39
4	16	9	277
5	30	23	1009
6	36	35	102
7	32	29	1542
8	88	91	180
9	32	24	261
10	22	18	1174
11	56	58	71
7 6 L			
0	15	11	983
1	94	92	1679
2	62	64	1699
3	48	47	1455
4	29	18	1324
5	30	32	290
6	14	24	66
7	64	63	248
8	18	20	211
9	26	18	1582
7 7 L			
0	58	63	0
1	12	20	320
2	42	46	1672
3	28	32	172
4	23	20	1747
5	22	17	1007
6	40	52	444
8 0 L			
2	123	125	1751
4	32	31	240
6	69	65	88
8	39	37	24
10	48	50	1688
12	69	67	1615
14	10	17	909
8 1 L			
0	82	77	1496
1	31	34	1721
2	24	24	1316
3	12	6	1519
4	29	27	578
5	26	26	1515
6	18	15	1371
7	16	12	777
8	30	27	1769
9	26	20	1140
10	18	8	1693
11	29	32	1520
12	25	27	107
13	50	53	1444
14	16	2	8
15	80	82	1789
8 2 L			
0	20	21	1281
1	18	16	1190
2	31	25	379
3	66	68	1602
4	6	18	410
5	34	37	1195
6	59	55	1770
7	19	15	1281
8	61	61	1695
9	79	79	69
10	56	57	1738
11	15	19	731
12	8	6	263
13	43	35	1496
14	42	44	32
8 3 L			
0	20	17	1699
1	12	17	1043
2	16	10	177
3	40	38	374
4	31	32	1748
5	61	62	328
6	18	13	154
7	74	73	91
8	96	95	165
9	22	27	1189
10	39	42	1767
11	36	38	1399
12	104	102	1718
8 4 L			
0	34	27	989
1	26	23	1789
2	75	78	185
3	17	25	1201
4	90	93	122
5	10	26	1283
6	32	32	1397
7	25	23	594
8	85	86	1739
9	15	15	226
10	3	16	774
11	33	30	259
8 5 L			
0	64	62	118
1	38	37	1538
2	63	58	235
3	13	18	1495
4	14	26	327
5	16	11	1391
6	48	48	106
7	22	29	1721
8	21	17	1331
9	27	32	1738
8 6 L			
0	50	52	207
1	16	10	1729
2	13	8	656
3	27	30	996
4	63	62	1753
5	31	34	128
6	18	23	0
9 0 L			
2	32	34	1441
4	27	27	1299
6	38	38	258
8	27	20	161
10	43	47	1453
12	43	43	1737
14	40	46	1146
9 1 L			
0	46	43	196
1	32	36	1247
2	64	66	70
3	22	22	445
4	12	5	357
5	19	31	1275
6	39	35	158
7	28	29	1378
8	27	24	1439
9	126	125	1782
10	51	48	376
11	14	14	1535
12	17	30	208
13	69	65	55
9 2 L			
0	12	14	1442
1	36	35	239
2	28	24	1558
3	78	81	192
4	28	32	1732
5	27	23	1693
6	59	59	57
7	72	71	1453
8	27	5	335
9	26	22	139
10	23	33	1637
11	58	53	538
12	16	5	8
9 3 L			
0	15	14	808
1	55	53	106
2	35	36	938
3	19	15	404
4	8	18	1051
5	60	56	1606
6	0	4	1578
7	26	22	1557
8	28	30	8
9	33	26	567
10	28	27	85
9 4 L			
0	61	63	1416
1	3	15	1375
2	3	20	1644
3	11	6	1789
4	55	56	490
5	31	37	427
6	25	25	1557
7	23	24	1724
8	47	55	1800
9	11	9	1423
9 5 L			
0	25	22	500
1	57	56	256
2	38	35	1409
3	23	8	1779
4	3	16	1692
5	57	67	1620
6	9	3	992
10 0 L			
2	23	22	196
4	45	43	1694
6	13	7	1531
8	15	3	1657
10	54	56	405
12	62	62	97
10 1 L			
0	41	43	20
1	59	54	1665
2	21	17	11
3	34	30	1627
4	16	6	825
5	34	36	377
6	71	68	104
7	53	53	167
8	19	27	696
9	40	39	108
10	16	24	1731
11	29	30	1574

L	FOBS	FCAL	ALPHA
10 2 L			
0	14	12	515
1	17	13	865
2	7	8	1124
3	55	55	1383
4	34	31	1739
5	61	60	1515
6	37	41	1551
7	27	20	1310
8	33	26	429
9	47	51	20
10	58	62	98
10 3 L			
0	17	21	282
1	24	28	1392
2	18	8	1381
3	3	20	1498
4	14	17	1760
5	32	40	268
6	17	8	1429
7	12	11	259
8	14	10	551
10 4 L			
0	46	48	1630
1	32	34	1688
2	98	102	1800
3	38	41	1371
4	20	6	630
5	11	6	897
11 0 L			
2	89	85	1776
4	3	20	1792
6	79	72	29
8	25	27	168
10	76	74	1740
11 1 L			
0	26	24	1371
1	16	14	1179
2	14	15	1736
3	44	41	1578
4	68	72	63
5	30	38	584
6	14	16	760
7	31	34	116
8	68	72	1708
9	28	30	409
11 2 L			
0	15	14	1660
1	17	18	671
2	3	6	1118
3	114	116	14
12 0 L			
4	53	59	164
5	28	27	206
6	24	18	304
7	23	14	1511
11 3 L			
0	24	6	1349
1	25	36	1425
2	18	37	91
3	26	28	1590
2	19	11	85
4	152	157	1760
6	41	30	1776
12 1 L			
0	31	24	1114
1	30	25	336
2	16	22	605
3	18	23	0
4	27	25	662
5	4	13	1248

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Fig. 8. Coordination polyhedron around Li(2).

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The Crystal and Molecular Structure of Vanadyldeoxophylloerythroetioporphyrin-1,2-dichloroethane Solvate: an Analogue of Chlorophyll*

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Single crystals of vanadyl deoxophylloerythroetioporphyrin-1,2-dichloroethane solvate, $C_{32}H_{34}N_4VO.C_2H_4Cl_2$, were grown by a vapor-phase diffusion technique. Pertinent crystal data are: space group $P2_1/a$, $a = 17.963$ (3), $b = 13.961$ (1), $c = 14.090$ (3) Å, $\beta = 116.97$ (1)°, $Z = 4$. The structure was solved by locating the position of the vanadium atom from a three-dimensional Patterson map and calculating successive Fourier series to locate the remaining atoms. A difference map revealed positions for 28 of the 38 hydrogen atoms, and these were used in the refinement procedure. Full-matrix least-squares calculations gave a final weighted R of 5·5% for approximately 2000 observed and unobserved reflections. The interesting feature of this molecule is the effect of the fifth isocyclic ring, E, on the porphyrin skeleton. Results indicate that this ring introduces strain into the molecule and causes distortions in the bond angles and most likely causes a shortening of the V–N bond to the ring C atom from an average of 2·10 Å for the other three V–N bonds to 1·96 Å for the shortened bond. The carbon and nitrogen atoms of the porphyrin skeleton are relatively planar and the vanadium atom lies 0·48 Å out of the plane of the four nitrogen atoms.

Introduction

In recent years new insights have been gained into the structure of chlorophyll and its related compounds. The basic structure of chlorophyll was worked out in the late 1930's by Hans Fischer (Fischer & Wenderoth,

1940) and subsequently confirmed through a very elaborate synthesis by R. B. Woodward and associates (Woodward, 1961). The accumulation of chemical information has recently made possible the description of the absolute configuration of chlorophyll *a* (Fleming, 1967). Crystallographers have shown an interest in an accurate structure determination for chlorophyll *a*, but the obstacle has so far been one of obtaining suitable crystals. At Mellon Institute an investigation has been begun into the feasibility of growing crystals of mater-