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Crystal Structure Refinement of Edingtonite

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Edingtonite, $Ba_{2\cdot02}Al_{4\cdot03}Si_{5\cdot97}O_{20}.7\cdot81H_2O$, a rare zeolite, is orthorhombic, space group $P2_12_12$, with $a=9\cdot550$ (10), $b=9\cdot665$ (10), $c=6\cdot523$ (5) Å. The structure was refined by least squares to a final R of 0·043 for 2158 observed reflexions ($R_w=0\cdot032$). The results obtained are consistent with the previously reported structural model. Eight water molecules per unit cell were located in the zeolitic channels and Si–Al ordering of the same kind as that found in natrolite was ascertained in the framework atoms. Two sets of crystallographically equivalent intersecting channels (free diameter 2·8 × 3·8 Å) lie in planes perpendicular to **c**. The structure of synthetic zeolite $Na^{ex}K$–F, a variant of the K–F phase, recently described as an edingtonite-type structure, could actually have a thomsonite-type of Si–Al ordering.

Introduction

Edingtonite is a rare barium zeolite first described in the basic effusive rocks near Old Kilpatrick, Dumbartonshire, Scotland (Haidinger, 1825). Only two more occurrences have been described: Böhlet Mine, Westergotland, Sweden (Nordenskjöld, 1895), and near Staré Ransko, eastern Bohemia (Novak, 1970). Edingtonite and other similar phases have recently been synthesized (Colella, 1973; Barrer, Beaumont & Colella, 1974).

Its ideal composition is $Ba_2Al_4Si_6O_{20}.8H_2O$. The chemical compositions of all the edingtonites are in very close agreement, the only disagreement being in the water contents which vary from $6H_2O$ (Strunz, 1970), to $7H_2O$ (Tschermak, 1918; Novak, 1970), to $8H_2O$ (Hey, 1934; Taylor & Jackson, 1933; Deer, Howie & Zussman, 1963).

The structure of natural edingtonite has been determined by Taylor & Jackson (1933) in the tetragonal space group $P\bar{4}2_1m$, though, on the basis of stoichiometry, these authors pointed out that the true symmetry was probably $P2_12_12$. In $P\bar{4}2_1m$ Taylor (1935) examined also the crystal structures of the Tl- and K-exchanged edingtonites. Bannister (in Hey, 1934) confirmed the orthorhombic symmetry of the Böhlet edingtonite, but with the Kilpatrick edingtonite he found tetragonal symmetry. Novak (1970) describes edingtonite from Staré Ransko as orthorhombic. On the basis of theoretical considerations Alberti & Gottardi (1975) confirm the highest symmetry of edingtonite to be orthorhombic, space group $P2_12_12$. Baerlocher & Barrer (1974) recently determined the structures of two variants of the synthetic zeolite K–F, namely $Na^{ex}K$–F and Rb–D, both based on the edingtonite-type framework.

The aim of this work was to determine the correct space group, to refine the structure, to locate the water molecules and to determine their number within the structure.

Experimental

A spheroidal fragment from Böhlet Mine, Westergotland, Sweden (specimen No. 1505 of Naturhistoriska Riksmuseets, Stockholm) was used.

New chemical data were obtained by atomic absorption for Na, K, Mg, Ca, Sr and Ba with a Perkin–Elmer 303 spectrophotometer; apart from Ba, all these elements are present only as traces, detectable but not measurable. The Si and Al contents are those reported by Van Reeuwijk (1972) for a sample from the same locality. Water loss was determined on approximately 10 mg of material by means of TG analysis with a thermal analyser manufactured by B.D.L. (Bureau de Liaison, Paris). The chemical formula and other crystal data are given in Table 1.

The cell dimensions, determined from 25 high-angle reflexions on a diffractometer, are in good agreement with those obtained by Bannister (Hey, 1934) for a sample from the same locality. Intensities were measured with a Philips PW 1100 four-circle computer-controlled diffractometer (Centro di Cristallografia Strutturale del CNR, Pavia, Italy), with Mo $K\alpha$ radia-

Table 1. *Crystal data*

Space group	$P2_12_12$
a	9·550 (10) Å
b	9·665 (10)
c	6·523 (5)
Cell volume	602·1 Å^3
Chemical formula	$Ba_{2\cdot02}Al_{4\cdot03}Si_{5\cdot97}O_{20}.7\cdot81H_2O$
D_m	2·78 (3) g cm^{-3}
D_x	2·80
λ(Mo $K\alpha$)	0·71069 Å
μ(Mo $K\alpha$)	39·1 cm^{-1}
Crystal size	0·14 × 0·18 × 0·20 mm
Number of independent reflexions	2266
Number of reflexions with $I>2\sigma(I)$	2158
Systematic absences	$h00$ with h odd $0k0$ with k odd

tion and the θ–2θ scan technique. 2283 reflexions within the range $2° < \theta < 35°$ were inspected with a scan rate of 0·04° θ/s and a symmetrical scan range of 1·0° in θ from the calculated diffraction angle.

Checking of diffraction intensities (absences $h00$: $h = 2n+1$ and $0k0$: $k = 2n+1$) confirmed the space group to be $P2_12_12$, in agreement with the piezoelectric behaviour noted by Wooster (Hey, 1934). 108 reflexions were considered to be 'unobserved' with $I < 2\sigma(I)$.

Processing of the data was carried out in the manner described by Davies & Gatehouse (1973). No absorption or extinction corrections were applied.

Refinement

The atomic coordinates given for $P\bar{4}2_1m$ by Taylor & Jackson (1933), adapted to $P2_12_12$, provided the initial coordinates for the refinement, which was carried out with a modified *ORFLS* full-matrix least-squares program (Busing, Martin & Levy, 1963) and electron density maps. Atomic scattering factors (Cromer & Mann, 1968) were used for Ba^{2+}, O^-, $Al^{1.5+}$ and Si^{2+} ($Al^{1.5+}$ was interpolated between Al and Al^{3+}, and Si^{2+} between Si and Si^{4+}). In the initial stage of the refinement a mean value for Al and Si, weighted in accordance with the chemical formula, was used for all tetrahedral positions in order to avoid any initial assumption about the Si–Al distribution. After two cycles of least squares a check on the (Al,Si)–O distances revealed one tetrahedron with longer distances than the rest. From this point on, the respective scattering factors for Al and Si were used.

Isotropic least-squares refinement converged to an R of 0·096, and R_w of 0·055, where $R = \sum||F_o| - |F_c||/$

Table 2. *Final atomic coordinates with their e.s.d.'s in parentheses*

For comparison, atomic parameters of Taylor & Jackson (1933), adapted from $P\bar{4}2_1m$ to $P2_12_12$, are given in italics below each parameter obtained in this study.

	Equipoint	x	y	z
Si(1)	2*a*	0	0	0·0140 (2)
		0	*0*	*0*
Si(2)	4*c*	−0·1759 (1)	0·0940 (1)	0·3884 (2)
		−0·186	*0·103*	*0·373*
Al	4*c*	0·0922 (1)	0·1714 (1)	0·6263 (2)
		0·103	*0·186*	*0·627*
O(1)	4*c*	0·1744 (3)	0·3311 (3)	0·6315 (5)
		0·167	*0·333*	*0·627*
O(2)	4*c*	−0·0530 (3)	0·1969 (3)	0·4673 (4)
		−0·056	*0·195*	*0·470*
O(3)	4*c*	0·1990 (3)	0·0369 (3)	0·5369 (4)
		0·195	*0·056*	*0·530*
O(4)	4*c*	0·0362 (3)	0·1329 (3)	0·8796 (5)
		0·047	*0·128*	*0·862*
O(5)	4*c*	−0·1341 (3)	0·0366 (3)	0·1574 (4)
		−0·128	*0·047*	*0·138*
Ba	2*b*	1/2	0	0·6299 (1)
		1/2	*0*	*0·623*
W(1)	4*c*	0·1748 (5)	0·3242 (5)	0·1421 (8)
		0·167	*0·333*	*0·129*
W(2)	4*c*	0·3811 (5)	0·1201 (5)	−0·0144 (7)
		0·397	*0·103*	*0*

Table 3. *Anisotropic temperature factors* (×10⁴), *dimensions and orientations of thermal ellipsoids*

The anisotropic temperature factor has the form: $\exp(-h^2\beta_{11} - k^2\beta_{22} - l^2\beta_{33} - 2hk\beta_{12} - 2hl\beta_{13} - 2kl\beta_{23})$. Principal vibrations (root mean square) are in Å; angles between crystallographic axes (a,b,c) and principal axes (U) of vibration ellipsoid are in degrees. Standard deviations are indicated in parentheses in terms of the last significant figures; the standard deviation for r.m.s. vibrations is 1 on the last digit.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	R.m.s. vib.	U^a	U^b	U^c	R.m.s. vib.	U^a	U^b	U^c	R.m.s. vib.	U^a	U^b	U^c
Si(1)	12 (1)	12 (1)	7 (3)	0 (2)	0	0	0·04	90	90	0	0·07	48	138	90	0·08	42	48	90
Si(2)	8 (1)	9 (1)	22 (2)	1 (1)	1 (1)	0 (1)	0·06	29	118	98	0·07	115	149	73	0·07	75	78	19
Al	11 (1)	7 (1)	15 (2)	−1 (1)	0 (2)	−1 (2)	0·06	85	59	31	0·06	104	145	59	0·07	15	105	86
O(1)	12 (2)	14 (2)	59 (6)	−7 (2)	−4 (5)	−1 (5)	0·05	40	51	84	0·10	52	141	83	0·11	99	88	10
O(2)	19 (3)	28 (3)	20 (6)	−8 (2)	−6 (4)	6 (4)	0·06	75	95	16	0·08	146	122	80	0·13	120	33	77
O(3)	24 (3)	15 (3)	44 (6)	9 (2)	−7 (4)	−12 (3)	0·06	110	33	65	0·09	131	84	138	0·13	48	57	121
O(4)	35 (3)	18 (2)	23 (5)	−2 (2)	5 (4)	−1 (4)	0·07	97	85	9	0·09	98	171	86	0·13	11	97	82
O(5)	20 (3)	35 (3)	16 (6)	0 (2)	5 (3)	−5 (3)	0·05	103	83	15	0·10	167	92	103	0·13	90	7	97
Ba	22 (1)	25 (1)	108 (1)	−5 (1)	0	0	0·09	35	55	90	0·12	55	145	90	0·15	90	90	0
W(1)	94 (6)	94 (6)	207 (13)	−19 (5)	47 (9)	−64 (9)	0·15	106	53	41	0·19	146	123	83	0·27	119	54	130
W(2)	109 (7)	110 (7)	219 (14)	21 (6)	15 (9)	−27 (9)	0·19	123	53	54	0·23	129	80	139	0·25	56	39	106

$\sum|F_o|$, and $R_w=[\sum w||F_o|-|F_c||^2/\sum w|F_o|^2]^{1/2}$ with $w=(1/\sigma_{Fo})^2$. At the end of the isotropic refinement, all populations, which were varied simultaneously with the thermal parameters, refined to the values of full occupancy.

Three further least-squares cycles with anisotropic temperature factors reduced R to 0·043 (omitting zeros) and 0·046 (including zeros), the weighted R_w being 0·032.

The final model was checked by a difference synthesis which showed no significant residual.

The crystallochemical results obtained at the end of the refinement are in good agreement with the data of the chemical analysis. The refinement in fact revealed 8·00 water molecules against the 7·81 water molecules found by chemical analysis.

Final atomic parameters are given in Table 2. Table 3 gives the anisotropic thermal parameters and their analysis. Bond distances and angles are listed in Table 4.* Fig. 1 is a projection of the structure on (001).

Results and discussion

The results are consistent with those of Taylor & Jackson (1933). As for all fibrous zeolites, the main feature is the presence of chains of SiO_4 and AlO_4 tetrahedra parallel to **c**. Each chain is laterally linked through O bridges to four neighbouring chains to form a three-

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31476 (17 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. *Interatomic distances* (Å) *and angles* (°)

Superscripts refer to the following positions:

None	x	y	z	viii	1/2-x	1/2+y	-z
i	x	y	z-1	ix	1/2-x	y-1/2	1-z
ii	x	y	z+1	x	1/2-x	y-1/2	-z
iii	-x	-y	z-1	xi	1/2+x	1/2-y	1-z
iv	-x	-y	z	xii	1/2+x	1/2-y	-z
v	1-x	-y	z	xiii	x-1/2	1/2-y	1-z
vi	1-x	-y	z+1	xiv	x-1/2	1/2-y	-z
vii	1/2-x	1/2+y	1-z				

Si(1)-tetrahedron

Si(1)-O(4^{I})	1.593(3) Å
Si(1)-O(4^{III})	
Si(1)-O(5)	1.625(3)
Si(1)-O(5^{IV})	
mean	1.609
O(4^{I})-O(4^{III})	2.661(6)
O(4^{I})-O(5)	2.607(4)
O(4^{III})-O(5^{IV})	
O(4^{I})-O(5^{IV})	2.616(4)
O(4^{III})-O(5)	
O(5)-O(5^{IV})	2.657(6)
O(4^{I})-Si(1)-O(4^{III})	113.2(2) °
O(4^{I})-Si(1)-O(5)	108.2(1)
O(4^{III})-Si(1)-O(5^{IV})	
O(4^{I})-Si(1)-O(5^{IV})	108.7(1)
O(4^{III})-Si(1)-O(5)	
O(5)-Si(1)-O(5^{IV})	109.7(2)

Si(2)-tetrahedron

Si(2)-O(1^{XIII})	1.608(3) Å
Si(2)-O(2)	1.622(3)
Si(2)-O(3^{IV})	1.609(3)
Si(2)-O(5)	1.654(3)
mean	1.623
O(1^{XIII})-O(2)	2.695(5)
O(1^{XIII})-O(3^{IV})	2.574(4)
O(1^{XIII})-O(5)	2.622(4)
O(2)-O(3^{IV})	2.693(5)
O(2)-O(5)	2.661(4)
O(3^{IV})-O(5)	2.649(4)
O(1^{XIII})-Si(2)-O(2)	113.2(2) °
O(1^{XIII})-Si(2)-O(3^{IV})	106.3(2)
O(1^{XIII})-Si(2)-O(5)	107.0(2)
O(2)-Si(2)-O(3^{IV})	113.0(2)
O(2)-Si(2)-O(5)	108.7(2)
O(3^{IV})-Si(2)-O(5)	108.5(2)

Al-tetrahedron

Al-O(1)	1.731(3) Å
Al-O(2)	1.749(3)
Al-O(3)	1.752(3)
Al-O(4)	1.776(4)
mean	1.752
O(1)-O(2)	2.747(4)
O(1)-O(3)	2.919(5)
O(1)-O(4)	2.834(4)
O(2)-O(3)	2.896(5)
O(2)-O(4)	2.888(5)
O(3)-O(4)	2.877(4)
O(1)-Al-O(2)	104.2(2) °
O(1)-Al-O(3)	113.8(2)
O(1)-Al-O(4)	107.8(2)
O(2)-Al-O(3)	111.6(2)
O(2)-Al-O(4)	110.0(2)
O(3)-Al-O(4)	109.2(2)

T-O-O angles

Si(1)-O(4^{I})-Al^{I}	138.3(2)
Si(1)-O(5)-Si(2)	142.0(2)
Si(2)-O(2)-Al	132.5(2)
Si(2^{IV})-O(3)-Al	134.8(2)

Ba-polyhedron

Ba-O(1^{IX})	2.889(3) Å
Ba-O(1^{XI})	
Ba-O(2^{IX})	3.040(4)
Ba-O(2^{XI})	
Ba-O(3)	2.960(4)
Ba-O(3^{V})	
Ba-W(1^{IX})	2.808(5)
Ba-W(1^{XI})	
Ba-W(2^{II})	2.832(5)
Ba-W(2^{VI})	

W(1)-polyhedron

W(1)-Ba^{VII}	2.808(5) Å
W(1)-O(1)	3.193(6)
W(1)-O(1^{I})	3.331(6)
W(1)-O(2)	3.278(6)
W(1)-O(3^{VII})	3.172(6)
W(1)-O(4^{I})	2.847(5)
W(1)-O(5^{XII})	2.993(6)
W(1)-W(2)	2.969(7)
W(1)-W(2^{VIII})	3.026(7)
W(1)-W(2^{XIV})	2.975(7)

W(2)-polyhedron

W(2)-Ba^{I}	3.040(4) Å
W(2)-O(4^{I})	3.368(7)
W(2)-O(4^{XI})	2.994(6)
W(2)-O(5^{IV})	3.019(6)
W(2)-W(1)	2.969(7)
W(2)-W(1^{X})	3.026(7)
W(2)-W(1^{XII})	2.975(7)
W(2)-W(2^{V})	3.247(10)

dimensional framework. Two sets of intersecting channels delimited by eight-membered rings run throughout the structure normal to **c**. The minimum free diameter of these channels is $2{\cdot}8 \times 3{\cdot}8$ Å, assuming the effective radius of O to be 1·35 Å (Fig. 2).

Ba^{2+} ions are located on the twofold rotation axes at $0,\frac{1}{2},z$ at the intersection of the channels, and are surrounded by six framework O atoms and four water molecules at an average distance of 2·906 Å. Of the six O atoms, however, four [two O(2) and two O(3)] are at a distance slightly above average from Ba, their distances being 3·04 and 2·96 Å respectively. The ordered arrangement of the Si and Al atoms first inferred by Taylor & Jackson (1933) has been fully confirmed. The average interatomic distances of 1·609 for Si(1)–O and 1·752 Å for Al–O do not differ significantly from the values of 1·603 and 1·761 Å quoted by Jones (1968) for a tetrahedron centred by only Si or only Al respectively, while the somewhat high value (1·623 Å) for the Si(2)–O bonds suggests some substitution of Si atoms by Al in this site. The ordered distribution of Si and Al in the chains of edingtonite is of the same kind as in natrolite chains.

The thermal vibration ellipsoids for the framework atoms are small, and for the Si and Al atoms are spherical within experimental error. Ba and O atoms and water molecules show a marked anisotropy, the longest axis of the thermal ellipsoid being consistently about double that of the shortest.

Recently Baerlocher & Barrer (1974) refined from powder data the structures of two variants of the synthetic zeolite K–F, namely Na^{ex}K–F ($a = 10{\cdot}056$, $c = 6{\cdot}680$ Å) and Rb–D ($a = 9{\cdot}978$, $c = 13{\cdot}215$ Å), both characterized by a Si/Al ratio of 1, and both having an edingtonite-type structure. It is highly probable that the structure of Na^{ex}K–F has the same Si–Al ordering as that found in the chains of thomsonite (which has a different linkage between the chains). Such a structure with an edingtonite framework and a thomsonite ordering was postulated by Alberti & Gottardi (1975). The same authors found that such a structure would have space group $P\bar{4}2_1c$ and cell dimensions: $a \simeq 9{\cdot}6$, $c \simeq 13{\cdot}2$ Å. Baerlocher & Barrer (1974) on the other hand pointed out that two weak lines of the Na^{ex}K–F pattern can only be indexed on the basis of a cell with a doubled c dimension. It is therefore possible that the Na^{ex}K–F variant of the synthetic zeolite K–F corresponds indeed to the theoretical edingtonite-type structure with thomsonite-ordering foreseen by Alberti & Gottardi (1975). On the other hand it is difficult to rule out the possibility that the doubling of c is due to the particular distribution of the cations within the channels.

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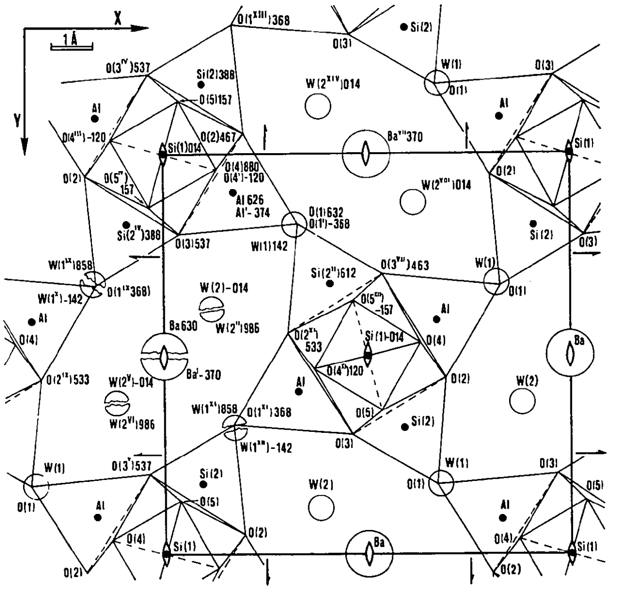

Fig. 1. Projection of the structure on (001). Numbers give the heights of the atoms in thousandths of the cell edge. Such numbers are given only for those atoms listed in Table 4.

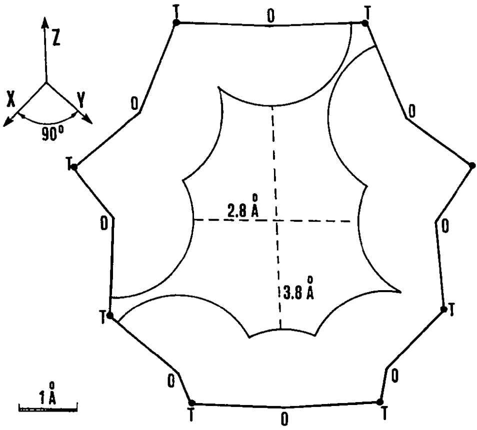

Fig. 2. Smallest cross section of a channel of edingtonite along [110]. The outer boundaries of oxygen ions are represented by circles of 1·35 Å radius.

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The Crystal and Molecular Structure of Bis[dihydrobis-(1-pyrazolyl)borato]nickel(II): Evidence for the Absence of Ni–H Interaction in Polypyrazolyl Borates of Nickel

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The crystal structure of bis[dihydrobis-(1-pyrazolyl)borato]nickel(II), $[H_2B(C_3N_2H_3)_2]_2Ni^{II}$, has been determined to a reliability index $R=0{\cdot}056$. The space group is *Pbca* with cell parameters $a=6{\cdot}331$ (2), $b=17{\cdot}485$ (7), and $c=14{\cdot}519$ (3) Å. The X-ray structure of this compound supports the recent hypothesis that the methylene H atoms of the bis[diethyl bis-(1-pyrazolyl)borato]nickel(II) complex do not act as apical ligands.

Introduction

Kosky, Ganis & Avitabile (1971) and Cotton, Jeremic & Shaver (1972) have reported an electronic interaction between the central metal and a nearby hydrogen in pyrazolyl borates of molybdenum, resulting in a stable 18-electron configuration and near octahedral geometry. The crystal structure of bis[diethyl bis-(1-pyrazolyl)borato]nickel(II) (Echols & Dennis, 1974) suggested that no such electronic interaction exists in this nickel complex. Although methylene H atoms occupy apical positions near nickel, there was no reason to propose that they were acting as ligands since there was no perturbation of the Ni–N bond lengths from the square planar values of analogous compounds (Nyburg & Wood, 1964). The present structure determination was undertaken to resolve the question of Ni–H interaction. The dihydro derivative serves as an excellent control for the comparison of Ni–N bond lengths.

Experimental

Red-orange crystals of bis[dihydrobis-(1-pyrazolyl)-borato]nickel(II), $[H_2B(C_3N_2H_3)_2]_2Ni^{II}$, were provided by Dr S. Trofimenko. Precession photographs showed systematic absences characteristic of the space group *Pbca*: $k=2n+1$ for $0kl$, $l=2n+1$ for $h0l$, and $h=2n+1$ for $hk0$; $h00$, $0k0$, and $00l$ reflections had absences of $h=2n+1$, $k=2n+1$, and $l=2n+1$ respectively.

Unit-cell dimensions (Table 1) were calculated by least-squares refinement of 2θ, ω, and χ settings for 15 independent reflections. Intensity data were collected on a Syntex $P\bar{1}$ computer-controlled diffractometer using molybdenum graphite-monochromatized radiation in the θ–2θ scan mode. Individual scan speeds were determined by a rapid scan at the calculated Bragg peak; the final scan rate varied from 2·0 to 24·0° min^{-1}. Background counts on each side of the peak were counted for $\frac{1}{4}$ the peak scan time. Three reflections were monitored 28 times during the data collection to check alignment and decomposition. Two symmetry equivalent sets of data (hkl and $hk\bar{l}$) were collected; equivalent reflections in these two sets showed no evidence of decomposition or the need for absorp-

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