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The Crystal and Molecular Structure of Sesqui(acetamide)(diacetamide)(perchlorato)lithium(I)

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The structure of sesqui(acetamide)(diacetamide)(perchlorato)lithium(I), $Li(CH_3CONH_2)_{1^1/_2}(CH_3CONHCOCH_3)ClO_4$, *has been determined from three-dimensional X-ray data. The unit cell is orthorhombic, space group Fdd2, having dimensions* $a = 13.742(5)$ Å, $b = 50.69(1)$ Å, $c = 7.854(1)$ Å, *and* $Z = 16$. *The intensity data were collected on an Enraf–Nonius CAD-4 automated diffractometer using monochromatic* CuK_α *radiation. The structure was determined by the heavy atom method and refined anisotropically to a conventional unweighted R-factor of 0.087.*

The compound is a structural dimer and contains octahedral lithium. The lithium ion is coordinated to six oxygens, two from the diacetamide, one from the perchlorate ion, and three from acetamides. The acetamide oxygens form bridges between two lithium ions. The coordination sphere about each lithium is a distorted octahedron, and the dimer consists of two of these octahedra having a face in common. Intermolecular hydrogen bonds exist between the diacetamide nitrogen and a perchlorato oxygen, linking the molecules in a three-dimensional network. Lithium–oxygen bond distances are 1.99–2.16 Å for the diacetamide and acetamide oxygens and 2.77 Å for the perchlorato oxygen. The Li–Li distance is 2.74 Å, indicating metal–metal interaction.

Introduction

Sesqui(acetamide)(diacetamide)(perchlorato)lithium(I), $LiClO_4 \cdot 1^1/_2A \cdot DA$, was a hydrolysis product in the attempted preparation of bis(diacetamide)(perchlorato)lithium(I), $LiClO_4 \cdot 2DA$. It was desired to prepare the latter compound for comparison with the analogous sodium structure, $NaClO_4 \cdot 2DA$, in which perchlorate ion was found to be coordinated to sodium[1]. If the perchlorate should complex with lithium, the structure would result in six-coordinate lithium, a rare occurrence in complexes of lithium with organic ligands. Since the properties under investigation were the coordination number of lithium and the possible coordination of perchlorate ion, the actual composition of the ligand was of secondary importance.

Experimental

Preparation

Stoichiometric amounts of diacetamide and anhydrous lithium perchlorate to form the compound $LiClO_4 \cdot 2DA$ were dissolved in methanol according to the method given by Gentile and Shankoff[2]. Crystals of alkali metal complexes are generally quite hygroscopic, so some degree of hydrolysis is not surprising. In the length of time (about two weeks) that it took for the crystals to form, some of the diacetamide had evidently decomposed to acetamide and acetic acid, resulting in the formation of $LiClO_4 \cdot 1^1/_2A \cdot DA$. Another attempt is being made to grow crystals of $LiClO_4 \cdot 2DA$ as well as crystals of $LiClO_4 \cdot 4A$ for further X-ray studies.

X-Ray Study

The colorless crystals were mounted inside glass capillaries for all X-ray measurements. Weissenberg photographs, using nickel-filtered copper radiation, showed the crystals belonged to the space group Fdd2, having cell constants $a = 13.742(5)$ Å, $b = 50.69(1)$ Å, $c = 7.854(1)$ Å, and $Z = 16$ ($d_{calc} = 1.44$ g/cm^3, $d_{obs} = 1.48$ g/cm^3). Intensity data collection was done on an Enraf-Nonius CAD-4 automated diffractometer using monochromatic CuK_α radiation. A total of 1727 reflections were collected of which 1256 were considered observed based on the criterion $I \geqq 1.5\sigma_I$.

Solution and Refinement

The structure was solved by the heavy atom method using computer programs obtained from the National Research Council of Canada[3]. The coordinates of atoms O_4 and C_7 (Figure 1) were restricted to the

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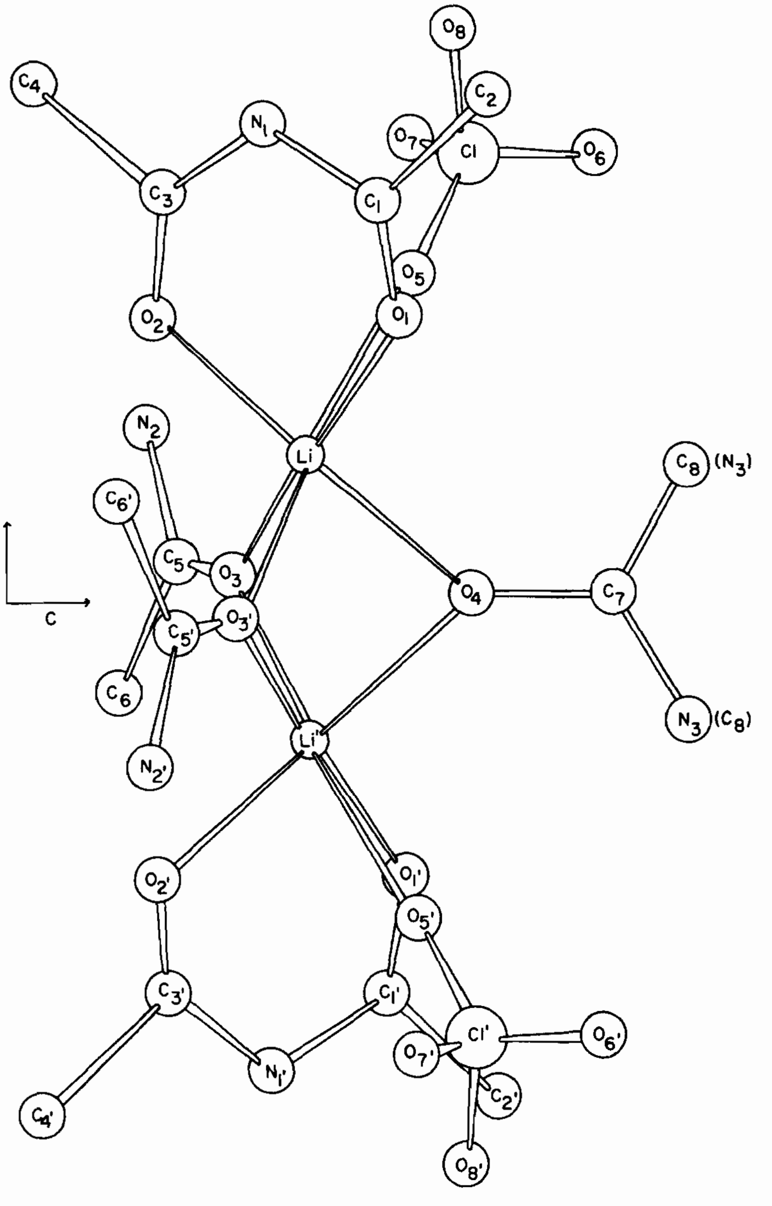

Figure 1. The dimeric unit.

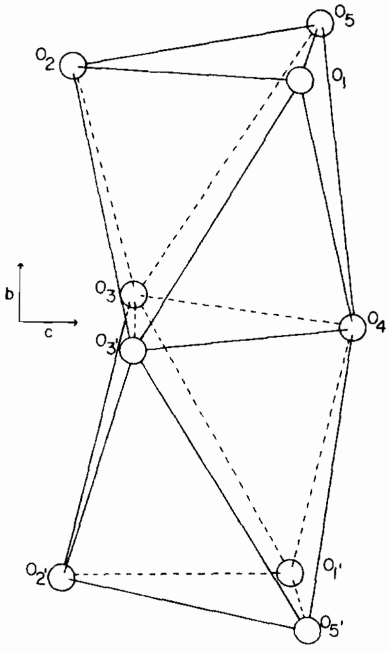

Figure 2. Coordination sphere of the dimeric unit.

special position 0, 0, z. The atoms N_3 and C_8 are disordered between equivalent positions related by a twofold axis, and an attempt to refine these two atoms individually was unsuccessful. Figures 1, 3, and 4 are drawn to show that although the mean position is known precisely, the assignment of the atoms as nitrogen or carbon cannot be made. A difference Fourier map was calculated but hydrogen atoms could not be located with any degree of certainty, and a final R-factor of 0.087 was obtained.

The mean atomic scattering factors had been corrected for both real and imaginary dispersion effects[4], and average values of the carbon and nitrogen scattering factors were used for the indeterminate atom during the later stages of refinement. The function minimized in the least squares calculation was $R = \Sigma w(|F_o| - k|F_c|)^2$, and the weighting scheme used was one based on counter statistics. Unobserved reflections were not included in the summations. A table of observed and calculated structure factors is available from the Editor. Fractional atomic coordinates and anisotropic thermal parameters are given in Tables I and II respectively.

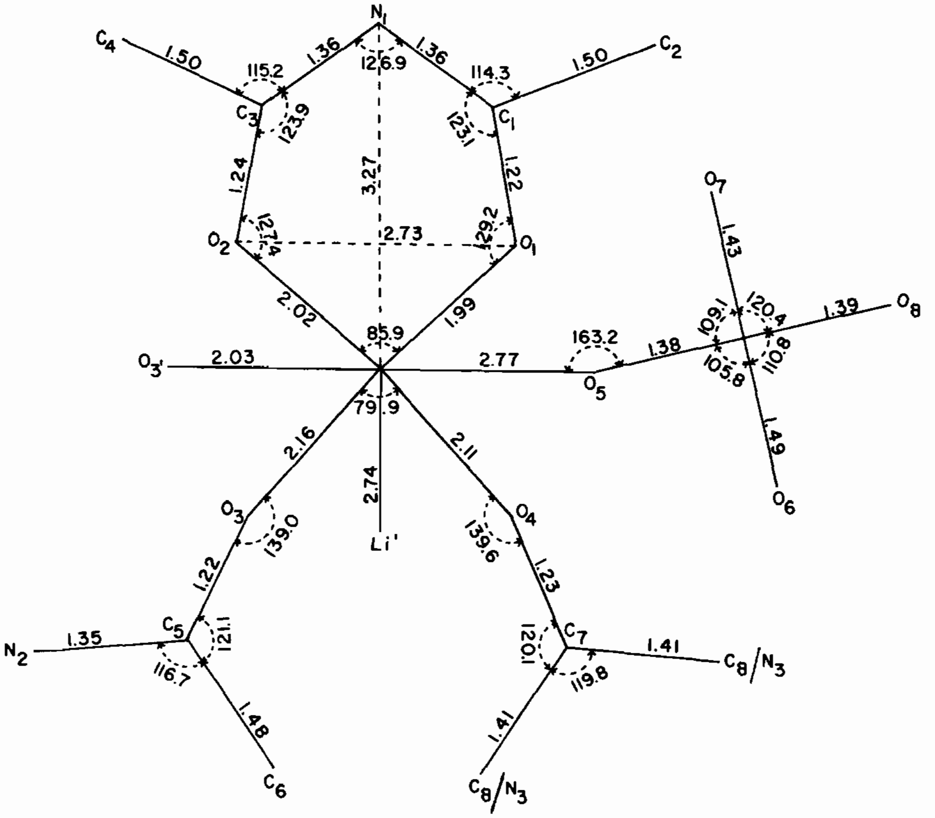

Figure 3. Interatomic distances and angles.

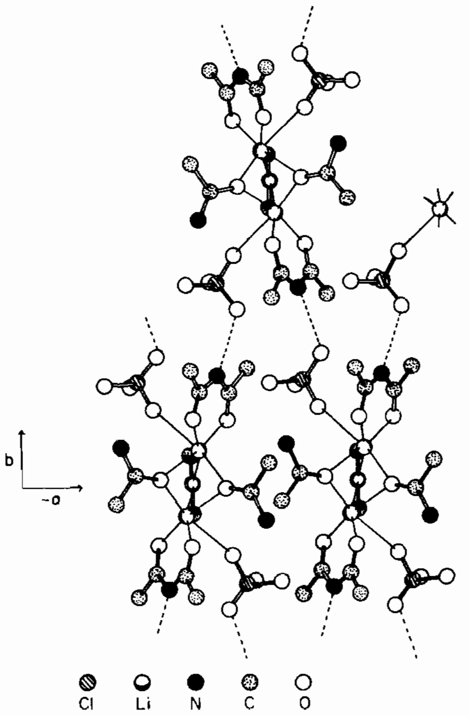

Figure 4. Packing diagram.

Results and Discussion

The molecular structure of sesqui(acetamide)(diacetamide)(perchlorato)lithium(I) is quite similar to that of bis(diacetamide)(perchlorato)sodium(I), Na ClO$_4$ · 2DA[1]. The lithium atom is six-coordinate, with the coordination sphere being a distorted octahedron. Although lithium is usually four-coordinate[5–7] in its complexes with organic ligands, at least one other complex containing octahedral lithium, LiI · 3ethylenediamine[8], has been reported, in which the lithium is bonded to six nitrogens.

Of the six oxygens making up the coordination sphere in LiClO$_4$ · 1$^1/_2$A · DA, one (O$_5$) is from the perchlorate ion, two (O$_1$,O$_2$) are from the diacetamide, and three (O$_3$, O$_3$', O$_4$) are from acetamides. The compound is a structural dimer, and the three acetamide oxygens form bridges between lithium ions, thus joining the two monomeric units, each of which may be represented empirically as LiClO$_4$ · 1$^1/_2$A · DA (Figure 1). The monomeric units are crystallographically equivalent, being related by a two-fold axis. The coordination sphere about each lithium is as octahedron distorted by elongation of the C$_4$ axis, and the dimer consists of two of these octahedra having a face in common (Figure 2).

TABLE I. Fractional Atomic Coordinates and Isotropic Thermal Parameters.

Atom	x/a	y/b	z/c	B
Li	−0.0194(9)[a]	0.0265(2)	−0.1864(15)	3.2
N_1	−0.0803(4)	0.0882(1)	−0.2422(9)	2.9
O_1	−0.1087(4)	0.0522(1)	−0.0765(7)	2.8
O_2	−0.0085(4)	0.0531(1)	−0.3767(7)	3.3
C_1	−0.1173(5)	0.0759(1)	−0.1021(10)	3.1
C_2	−0.1707(8)	0.0938(2)	0.0180(14)	5.3
C_3	−0.0295(5)	0.0768(1)	−0.3713(10)	3.0
C_4	0.00001(8)	0.0952(2)	−0.5121(13)	6.3
O_3	0.1010(3)	0.0035(1)	−0.2816(7)	2.9
C_5	0.1776(5)	0.0069(1)	−0.3558(10)	3.3
C_6	0.2349(6)	−0.0156(2)	−0.4200(13)	6.5
N_2	0.2147(5)	0.0313(1)	−0.3842(13)	3.7
O_4	0.0	0.0	0.0182(9)	4.0
C_7	0.0	0.0	0.1785(12)	4.0
C_8/N_3	0.0025(6)	0.0240(2)	0.7685(11)	6.0
Cl	0.1631(2)	0.08415(3)	0.0001(4)	4.2
O_5	0.1153(7)	0.0614(1)	−0.0502(18)	7.6
O_6	0.1836(8)	0.0808(3)	0.1848(13)	12.3
O_7	0.2607(7)	0.0834(3)	−0.0618(15)	11.3
O_8	0.1053(7)	0.1061(1)	−0.0281(20)	8.2

[a] Estimated standard deviations, given in parentheses, are right-adjusted to the least significant digit in the preceding number.

TABLE II. Anisotropic Thermal Parameters as Mean Square Amplitude[a] for $LiClO_4\cdot 1^1/_2A\cdot DA$.

Atom	$U_{11}\times 10^3$	$U_{22}\times 10^3$	$U_{33}\times 10^3$	$U_{23}\times 10^3$	$U_{13}\times 10^3$	$U_{12}\times 10^3$
Li	57(8)[b]	38(5)	38(6)	6(10)	3(1)	7(11)
N_1	57(3)	26(3)	37(3)	6(6)	14(6)	−5(5)
O_1	66(3)	37(3)	48(3)	18(4)	27(5)	16(4)
O_2	69(3)	39(3)	52(3)	12(6)	37(6)	24(4)
C_1	48(4)	39(3)	42(4)	−14(6)	2(7)	5(6)
C_2	105(7)	61(4)	70(6)	−52(10)	86(12)	24(9)
C_3	50(4)	46(4)	36(4)	16(6)	4(7)	9(6)
C_4	124(8)	51(4)	78(7)	47(10)	109(14)	5(9)
O_3	39(3)	35(3)	58(3)	8(4)	27(5)	1(4)
C_5	34(4)	46(4)	42(4)	2(6)	4(7)	1(5)
C_6	57(5)	57(4)	83(7)	−30(10)	52(9)	21(7)
N_2	68(5)	56(4)	116(7)	−2(6)	88(10)	−33(6)
O_4	67(5)	52(4)	26(3)	0	0	16(6)
C_7	41(6)	38(7)	28(5)	0	0	8(9)
C_8/N_3	96(6)	79(5)	51(4)	−63(6)	−14(9)	3(8)
Cl	64(1)	46(1)	78(1)	−10(2)	−12(2)	−11(2)
O_5	128(7)	68(4)	254(14)	−75(12)	−184(16)	4(8)
O_6	159(8)	260(13)	81(6)	−28(16)	5(12)	69(2)
O_7	100(6)	250(12)	130(9)	42(18)	73(13)	3(15)
O_8	154(8)	56(4)	331(18)	−34(16)	−267(21)	48(9)

[a] The form of the anisotropic thermal parameter is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)]$. [b] Estimated standard deviations, given in parentheses, are right-adjusted to the least significant digit in the preceding number.

The two bridged lithium ions are separated by a distance of 2.74Å. This is in good agreement with the corresponding distance (2.71Å) in $LiClO_4 \cdot 3H_2O$[9] and somewhat larger than the Li–Li distance (2.585Å) in $LiIO_3$[10]. However, there is a greater degree of distortion of the coordination sphere in $LiIO_3$ than in either $LiClO_4 \cdot 3H_2O$ or $LiClO_4$ $1^1/_2$A·DA. It should also be noted that the Li–Li distance in $LiClO_4 \cdot 1^1/_2$A·DA is only slightly longer than that found in Li_2 (2.68Å)[11], indicating metal–metal interaction.

The diacetamide is in the *anti–anti* comformation, and is very nearly planar. The distortion observed in the $NaClO_4 \cdot 2$DA complex, *i.e.* a fold along the metal–nitrogen axis, is virtually non-existent in $LiClO_4 \cdot 1^1/_2$A·DA. The dihedral angle between planes O_1–C_1–N_1 and O_2–C_3–N_1 in the latter compound is only 1.2°. The bite of the diacetamide (2.73Å) is almost identical with those found in $NaClO_4 \cdot 2$DA (2.74, 2.76Å). The acetamides are planar, and all bond distances and angles within the ligands are comparable to those for crystalline acetamide[12]. The only discrepancies are found in the acetamide lying on the two-fold axis and are a result of using average values in calculating the position of the indeterminate atom.

Besides six-coordinate lithium, the other important feature of this structure is the coordination of the perchlorate ion. The sum of the ionic radii of lithium and oxygen (2.08) and the sum of the atomic radii (2.05Å) are almost identical[13], so from the observed distances, no conclusion can be drawn regarding the degree of covalent character of the Li–O bond. The Li–O_5 distance (2.77Å) is significantly greater than the other Li–O distances (1.99–2.16Å). On the basis of the ionic radius of lithium, there is considerable crowding of the four planar oxygens and the perchlorato oxygen is as close as possible (~2.8Å) to the lithium. The lithium ion is actually 0.20Å below the plane formed by O_1, O_2, O_3, and O_4, while O_5 is 2.57Å above this plane. The Li–O_5 distance is much greater than the sum of either the atomic or the ionic radii of lithium and oxygen, but all other Li–O distances are very close to this sum. The isotropic thermal parameter of O_5 is low, as would be expected for a rigidly held atom.

TABLE III. Interatomic Distances (Å) for $LiClO_4 \cdot 1^1/_2$A·DA.

Bond Distances in Coordination Sphere			
Li–O_1	1.99(1)[a]	Li–O_4	2.11(3)
Li–O_2	2.02(1)	Li–O_5	2.77(2)
Li–O_3	2.16(1)	Li–$O_{3'}$	2.03(1)[b]
Bond Distances within Ligands			
N_1–C_1	1.363(10)	O_3–C_5	1.215(8)
N_1–C_3	1.359(10)	C_5–C_6	1.476(11)
C_1–O_1	1.221(8)	C_5–N_2	1.353(9)
C_3–O_2	1.237(8)	O_4–C_7	1.259(12)
C_1–C_2	1.501(12)	C_7–C_8/N_3	1.409(9)
C_3–C_4	1.502(12)		
Bond Distances within Perchlorato Group			
Cl–O_5	1.387(8)	Cl–O_7	1.428(10)
Cl–O_6	1.488(10)	Cl–O_8	1.385(8)
Pertinent Non-bonded Distances			
Li–Li′	2.735(16)	C_1–C_3	2.434(11)
Li–N_1	3.268(12)	Li–Plane	–0.200(10)
O_1–O_2	2.731(8)	Cl–Plane	2.557(13)
O_2–O_3	3.024(6)		
O_3–O_4	2.739(8)		
O_4–O_1	3.129(5)		
Hydrogen Bonded Distance			
N_1–O_8*	2.972(8)[c]		

[a] Estimated standard deviations, shown in parentheses, are right-adjusted to the least significant digit in the preceding number. [b] Primes refer to atoms at the equivalent positions –x, –y, z relative to the asymmetric unit x, y, z. [c] Asterisk refers to atoms at the equivalent position $^1/_4$+x, $^1/_4$–y, $^1/_4$+z relative to the asymmetric unit x, y, z.

TABLE IV. Bond Angles (°) for $LiClO_4 \cdot 1^1/_2A \cdot DA$.

Angles Involving Lithium			
O_1–Li–O_2	85.9(5)[a]	Li–$O_{3'}$–Li′	81.5(5)
O_2–Li–O_3	92.7(5)	O_1–Li–O_3	168.0(7)
O_3–Li–O_4	79.9(4)	O_2–Li–O_4	168.3(7)
O_4–Li–O_1	99.5(5)	$O_{3'}$–Li–O_1	108.0(6)
O_5–Li–O_1	80.0(5)	$O_{3'}$–Li–O_2	105.6(6)
O_5–Li–O_2	79.1(5)	$O_{3'}$–Li–O_3	83.8(5)
O_5–Li–O_3	88.1(5)	$O_{3'}$–Li–O_4	82.8(5)
O_5–Li–O_4	91.6(5)	$O_{3'}$–Li–O_5	170.8(6)
Li–O_5–Cl	163.2(7)	Li–O_3–C_5	139.0(5)
Angles within Ligands			
O_1–C_1–N_1	123.1(6)	N_1–C_3–C_4	115.2(6)
O_1–C_1–C_2	122.6(7)	O_3–C_5–N_2	122.3(7)
N_1–C_1–C_2	114.3(7)	O_3–C_5–C_6	121.1(7)
C_1–N_1–C_3	126.9(6)	N_2–C_5–C_6	116.7(7)
O_2–C_3–N_1	123.9(6)	O_4–C_7–C_8/N_3	120.1(6)
O_2–C_3–C_4	121.0(6)	C_8/N_3–C_7–C_8/N_3	119.8(6)
Angles within Perchlorato Group			
O_5–Cl–O_6	105.8(6)	O_6–Cl–O_7	98.7(7)
O_5–Cl–O_7	109.1(6)	O_6–Cl–O_8	110.8(7)
O_5Cl–O_8	110.6(6)	O_7–Cl–O_8	120.4(7)
Dihedral Angles			
O_2–C_3–N_1 and O_1–C_1–N_1	1.2		
O_1–C_1–C_3–O_2 and C_1–N_1–C_3	0.4		

[a] Estimated standard deviations, shown in parentheses, are right-adjusted to the least significant digit in the preceding number.

The complex is bonded intermolecularly via hydrogen bonds between a perchlorato oxygen (O_8) and the diacetamide nitrogen. Each dimeric unit is linked to two above and two below, forming a three-dimensional network throughout the unit cell (Figure 4).

The infrared spectrum shows peaks characteristic of a perchlorato group having C_{2v} symmetry[14]. The stretching frequencies occur at 970, 1045, 1125, and 1200 cm^{-1} and are in agreement with those found for other bidentate perchlorates[15, 16].

All pertinent interatomic distances and angles are found in Tables III and IV and in Figure 3. A packing diagram is given in Figure 4.

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