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INVESTIGATIONS OF ALKALINE-EARTH β-DIKETONE COMPLEXES. I. THE CRYSTAL AND MOLECULAR STRUCTURE OF BIS(DIMETHYLFORMAMIDO) BIS(1, 3-DIPHENYL-1, 3-PROPANEDIONATO)MAGNESIUM

Frederick J. Hollander, David H. Templeton
and Allan Zalkin

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Investigations of Alkaline-earth β-diketone Complexes. I. The crystal and molecular structure of bis(dimethylformamido)bis (1,3-diphenyl-1,3-propanedionato)magnesium*

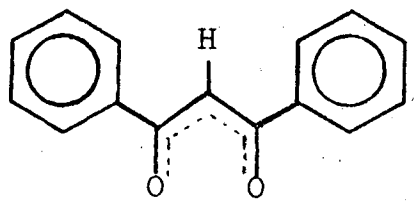
By Frederick J. Hollander, David H. Templeton and Allan Zalkin
Lawrence Berkeley Laboratory and Department of Chemistry,
University of California, Berkeley, California 94720 U.S.A.

Bis(dimethylformamido)bis(1,3-diphenyl-1,3-propanedionato) magnesium, $(DMF)_2(DPP)_2Mg$, $MgC_{36}H_{36}N_2O_6$, is monoclinic, space group $\underline{C}2/\underline{c}$, with $\underline{a}$ = 16.893(3) Å, $\underline{b}$ = 12.853(2) Å, $\underline{c}$ = 16.927(3) Å, β = 117.085(5)° at 23°C, $\underline{Z}$ = 4, $\underline{d_c}$ = 1.10 g/cm^3. The structure was determined by direct methods and refined to $\underline{R}$ = 0.067 for 1817 independent reflections measured with a scintillation counter using a θ-2θ scan. Each magnesium is octahedrally coordinated by the oxygen atoms of two DMF and two diketone molecules. The complex is monomeric and is situated on a 2-fold axis with the two DMF molecules <u>cis</u> to each other. Some remarks are made on distortions of ligand octahedra.

*Work performed under the auspices of the U.S. Atomic Energy Commission.

Introduction

Alkaline-earth ions are known to make complexes with various diketones, but few crystal structures of the compounds have been reported. We became interested in these substances and have investigated several complexes of 1,3-diphenyl-1,3-propanedione anion (DPP):



(–)

With Mg, Ca and Sr as cations we obtained suitable crystals only when certain solvent molecules were involved in the coordination.

This first paper reports the structure of $Mg(DPP)_2(dimethylformamide)_2$. The magnesium ion is octahedrally coordinated. The complex occurs as a monomeric unit possessing a crystallographic two-fold axis. The two neutral dimethylformamide solvent molecules are cis to one another and have bond lengths from the oxygen to the magnesium that are significantly longer than those from the DPP oxygens to the magnesium.

Experimental Procedure

The compound was synthesized by combining an aqueous solution of magnesium acetate and an ethanolic solution of 1,3-diphenyl-1,3-propanedione (HDPP) in a strong

NH_3/NH_4Cl, pH 10, buffer. All materials used were of reagent grade and were not further purified before use. A pale yellow precipitate formed immediately, and the mixture was stirred for several hours before the precipitate was filtered and dried in air. The filtrate, on standing, yielded another precipitate which was filtered and shown by its powder pattern to be identical to the first.

Attempts were made to recrystallize the compound from various organic solvents and mixtures. Recrystallization from ethanol yielded crystals which decomposed rapidly, even in sealed capillaries. Precession photographs of these crystals were so poor that they could not be indexed. Evaporation in air of dimethylformamide (DMF) solutions of the compound yielded very good crystals which were used throughout the rest of this investigation. These crystals still tended to decompose on exposure to air, but were stable in sealed capillaries and in a desiccator over Drierite. The crystals were also stable in air during one period of very low humidity, which suggests that moisture is responsible for the decomposition. A powder pattern of the recrystallized material was different from that of the original precipitate, but after exposure to air the diffraction lines of the original material slowly reappeared.

Several crystals were mounted in sealed quartz capillaries for study. Weissenberg and precession photographs indicated a monoclinic unit cell with absences $\underline{hk\ell}$, $\underline{h} + \underline{k}$ /

$2\underline{n}$ and $\underline{h}0\ell$, $\ell \neq 2\underline{n}$. These absences are consistent with space groups $\underline{Cc}$ or $\underline{C}2/\underline{c}$, with $\underline{b}$ as the unique axis; solution of the structure confirmed $\underline{C}2/\underline{c}$ as the space group.

Further measurements were made with a General Electric XRD-5 manual three-circle diffractometer, and twelve high-angle reflections were carefully centered using Cu $\underline{K}\alpha_1$ radiation (λ = 1.54051 Å). The cell dimensions were refined on the 2θ measurements only, using program TTHCEL, a modification of a least-squares program supplied to us by H. Hope. The cell parameters and their standard deviations as given by least squares are $\underline{a}$ = 16.893(3) Å, $\underline{b}$ = 12.853(2) Å, $\underline{c}$ = 16.927(3) Å, β = 117.085(5)°, at 23°C. The density was not measured due to difficulty in finding a suitable flotation medium. The calculated density for an empirical formula $Mg(DPP)_2$ gave $\underline{Z}$ = 4, $\underline{d}_{\underline{c}}$ = 0.96 gm/cm^3 as the most reasonable result. The density based on the actual composition of $Mg(DPP)_2(DMF)_2$ with $\underline{Z}$ = 4 is $\underline{d}_{\underline{c}}$ = 1.10 gm/cm^3.

Intensity data were collected from a crystal of approximate dimensions 0.25 mm x 0.25 mm x 0.30 mm sealed in a quartz capillary and mounted on a Picker/Nuclear four-circle diffractometer automated by a DEC PDP 8I computer and disc, using graphite monochromatized ($2\theta_{\underline{m}}$ = 26.36°) Cu $\underline{K}\alpha$ radiation. Intensities were collected using a θ-2θ scan technique at an X-ray tube takeoff angle of 3°. Peaks were

scanned at a rate of 1°/min from 0.9° below the predicted $K\alpha_1$ position to 0.9° above the predicted $K\alpha_2$ position. Backgrounds were counted for 10 seconds at positions offset 0.6° from each end of the scan interval (all angles in 2θ). Aluminum attenuators were automatically inserted in the diffracted beam whenever the count rate exceeded 10000 cps, and the peak and backgrounds were remeasured with the attenuators in place. The reflections (4 0 0), ($\bar{2}$ 0 2) and (0 4 $\bar{4}$) were monitored periodically during the data collection and exhibited no decay in intensity. All reflections in the quadrant of reciprocal space $+h, +k, \pm \ell$ were measured out to a 2θ angle of 120° ($\sin\theta/\lambda < 0.562$). 2433 unique reflections were measured, of which 614 had $I < \sigma(I)$. Net intensities and their standard deviations were calculated by the formulae:

$$I = C - \frac{t_c}{2t_b}(B_1+B_2) \qquad \sigma^2(I) = C + \frac{t_c^2}{4t_b^2}(B_1+B_2)$$

where C is the total counts measured over scan time t_c and B_1 and B_2 are the background counts, each measured for time t_b. No absorption correction was performed ($\mu = 7.7\ cm^{-1}$). Intensities of equivalent reflections and those measured more than once were averaged. Standard deviations were set equal to the greater of $(1/n)(\Sigma\sigma_i^2)^{1/2}$ or $[1/(n-1)](\Sigma\Delta_i^2)^{1/2}$, where σ_i and Δ_i are the standard

deviation of the ith measurement and the deviation of the ith measurement from the average respectively, and n is the number of reflections averaged. Lorentz and polarization factors were applied.

The scattering factors of Doyle and Turner (1968) were used for neutral Mg, C and O, together with the real and imaginary dispersion terms of Cromer and Liberman (1970). The spherical hydrogen scattering factors of Stewart, Davidson and Simpson (1965) were used.

Our least-squares program minimizes the function $\Sigma w(\Delta F)^2/\Sigma wF_o^2$. The weighting scheme used throughout the refinement gave zero weight if $F^2<\sigma(F^2)$, and $w = 1/\sigma(F)$ otherwise. Finite differences were used to calculate $\sigma(F)$ from $\sigma(F^2)$ and F^2:

$$\sigma(F) = F - (F^2-\sigma(F^2))^{1/2} \; ; \quad \sigma^2(F^2) = \sigma_c^2(F^2) + (pF^2)^2$$

where p is a factor (equal 0.06 in the final cycles) used to reduce the weights of intense reflections, which are more prone to undetected systematic errors, and $\sigma_c(F^2) = (Lp)^{-1}\sigma(I)$.

The following programs, written for our CDC 6600 computer, were also used in the solution and refinement of this structure: MAGPIK, a program for interpretation of raw data from the Picker/DEC system; INCOR, EDIT, and ORDER, general data reduction programs; WILSON, an unpublished program written by Maddox and Maddox for applying Wilson's (1942) statistics

to data and calculation of normalized structure factors; REL, R. E. Long's (1965) program for direct determination of centric phases; FORDAP, A. Zalkin's Fourier analysis program; LSLONG, our modification of the Ganzel-Sparks-Trueblood least-squares program; DISMAT, a crystallographic distances and angles program which calculates standard deviations using the correlation matrix from least-squares; ORTEP, C. Johnson's (1965) thermal ellipsoid plotting program; LSPLAN, our modification of the least-squares planes program from the University of Pittsburgh; and LIST1 and LISTAP, data presentation programs.

Structure Determination and Refinement

Normalized structure factors, E_h, were calculated using Wilson's (1942) method. Analysis of the average values of E and E^2-1 strongly indicated the centric space group (ave(E) = 0.792 vs. 0.792 (0.886) and ave $|E^2-1|$ = 0.973 vs. 0.968 (0.736) theoretical values for the centric and (acentric) case). Since the most probable number of molecules in the unit cell was four according to density considerations, this implied that the Mg atom had to lie either on the two-fold axis at $x = 0$, $z = 1/4$ or on a center of symmetry (0,0,0 or 1/4,1/4,1/4) in the eight-fold space group.

REL, R. E. Long's (1965) sign determination program was used in the attempt to determine the phases of the 316 reflections with $E > 1.50$. After some failures, we found an

E-map which could be interpreted as a superposition of two non-centric structures. Selected atoms were refined by least-squares and Fourier methods, in space group Cc, until with 45 atoms $R_1 = \Sigma|\Delta F| / \Sigma|F_o|$ was reduced to 0.16, and a difference Fourier showed no peaks greater than 0.5 $e/Å^3$. Refinement proceeded slowly. At this point the structure consisted of $Mg(DPP)_2$ and two molecules of DMF in the asymmetric unit.

Then it was noticed that the $Mg(DPP)_2(DMF)_2$ complex possessed a non-crystallographic (in Cc) two-fold axis in the y direction and that the z of the Mg atom was very close to 0.25. The poor behavior of the refinement was thus explained, since supposedly unrelated parameters were actually heavily correlated. The structure was fitted to the centric group by changing the x coordinates of all the atoms and averaging the two-fold related positions. Three cycles of centric full-matrix least-squares refined quickly and with only small shifts to an R_1 of 0.154. The results of the Wilson statistics and the excellent refinement of the structure in the centric space group confirm that choice.

All of the atoms were then allowed to refine with anisotropic thermal parameters, and the R_1 reduced to 0.141. In further refinement the factor p was included in the weighting. Most of the hydrogen atoms were located by a sequence of difference Fourier calculations. The hydrogens attached to C(17) did not refine well in least-squares, and they were

included in the last calculations with fixed positions and thermal parameters. All other hydrogens were refined independently with isotropic thermal parameters. In the last cycle of least-squares all parameter shifts were less than 10% of their standard deviations. The final R_1 was 0.067 for 1817 reflections. The final $R_2 = (\Sigma w(\Delta F)^2/\Sigma wF_o^2)^{1/2}$ was 0.065 and the standard deviation of an observation of unit weight was 1.30. The data were checked for secondary extinction with negative results.

Values of F_o and the final differences are given in Table 1. The final coordinates and thermal parameters of the atoms are given in Table 2.

Results and Discussion

The structure is separated into well-defined complex groups with composition $Mg(DPP)_2(DMF)_2$. The magnesium has a formal charge of +2 and each of the DPP ligands has a formal charge of -1; the DMF molecules are formally neutral. The magnesium is in a special position on the two-fold axis, and is coordinated by two symmetry-related DPP and two symmetry-related DMF molecules. The two DPP ligands lie above and to either side of the magnesium in such a way that their mean planes form a propeller around a two-fold axis. The planes of the two DMF molecules are so oriented that there is no indication of a propeller in their configuration (Fig. 1).

The six oxygen atoms coordinating the magnesium lie on the corners of a slightly distorted octahedron. The distances from the magnesium to the oxygens in the DPP ligand are identical to within a standard deviation, at 2.055(2) Å and 2.057(3) Å, while the Mg-O distance to the DMF is slightly, but significantly, longer at 2.095(3) Å. Both of these distances fall well within the range for typical Mg-O distances in the literature (2.0 Å - 2.15 Å), with the Mg-O(DPP) distance being shorter than the Mg-O(DMF) as expected from electrostatic interactions. The angles of the octahedron are also distorted (Table 3). The angle O(2)-Mg-O(2)' is concave upward in Fig. 1, and the O(1)-Mg-O(1)' and O(3)-Mg-O(3)' planes are twisted out of perpendicularity to this plane (Fig. 2).

The distances between oxygens coordinating the Mg range from 2.81 Å to 3.07 Å, with the minimum distance being between the two oxygens in the same DPP ligand. There are several close C--O and C--C contacts within the complex, specifically across the two-fold axis, due to the close bonding of the oxygens to the magnesium. Analysis of the least-squares planes through portions of the molecules involved shows that the DPP is pushed away from the two-fold axis so that the Mg atom is 0.58 Å above the least-squares plane of the diketone and that the DMF molecules are spread away from the axis so that Mg is above that molecular plane by 0.29 Å. (The distances given are the perpendicular distances to the plane involved. "Above" implies that the distance from the plane to the Mg has a component upward in Fig. 1.)

The two phenyl groups, the diketone ring and the DMF molecule are each planar to within five standard deviations of the coordinates of the atoms involved. The two phenyl rings are twisted with respect to the diketone plane by 47.6° and 30.9° for the first (C(1)-C(6)) and second (C(10)-C(15)) rings respectively. The first phenyl ring is also bent so that C(6) is out of the diketone plane by 0.08 Å.

The average C-C distance in the phenyl rings is 1.376 Å. Other bond distances in the DPP and DMF molecules are as expected (Williams, 1966; Hollander, 1972; Sutton, 1958). The O-C-C and C-C-C angles in the diketone are spread (ave. 125°) as expected, to give the ligand a bigger bite. In the phenyl groups the interior angle nearest the diketone is significantly less than the ideal 120° (118.8° and 117.5° for the first and second phenyls respectively). The phenyl C-C bond distances to the <u>para</u> carbon atoms are also systematically shorter than the C-C bond distances to the other carbons (Table 4).

The complexes themselves are packed in an interlocking manner shown in Fig. 3. The phenyl rings extending away from the two-fold axis (C(10)-C(15)) project into the open space between the other two phenyl rings of a <u>C</u>-centering related complex and the DMF molecules of the complex related to the second by a translation in <u>y</u>. The phenyl rings directed up the two-fold axis with respect to the Mg project

into the area just below the DMF molecules of the complex above it. The phenyls also project into the relatively open area to the side of a complex related to it by a center of symmetry, and the DMF ligands into the open side of a complex related by the n glide at y = 1/4.

There are only three short (<3.50 Å) inter-complex contacts between non-hydrogen atoms. They are 3.39 Å from O(1) to a C(18) of the complex related to the first by the n glide at y = 1/4, 3.48 Å from O(2) to a C(2) of the complex related by the center of symmetry at 0,1/2,1/2 and 3.34 Å from C(4) to a C(4) of the complex related by the n glide at y = 3/4.

The octahedral coordination of Mg in $Mg(DPP)_2(DMF)_2$ is similar to that exhibited by other β-diketone complexes of divalent metals, e.g. diaquobis(acetylacetonato)-magnesium, $Mg(AA)_2(H_2O)_2$ (Morosin, 1967), $Co(AA)_2(H_2O)_2$ (Bullen, 1959), and $Ni(AA)_2(H_2O)_2$ (Montgomery and Lingafelter, 1963). In each case, the divalent metal cation is octahedrally coordinated by two β-diketone ligands and two solvent molecules in a monomeric unit. In all of these cases, the oxygen atoms in the solvent molecules are significantly further away from the metal ion than are the ligand oxygen atoms. For the $Mg(DPP)_2$ complex, the distortion (2.06, 2.06, 2.10 Å) is similar to the distortion for the acetylacetonato complexes of Mg (2.03, 2.04, 2.15 Å), Co (2.05, 2.06, 2.23 Å)

and Ni (2.02, 2.01, 2.14 Å). This effect is also noted in a dimeric situation with octahedral coordination in $Co(AA)_2(H_2O)$ (Cotton and Elder, 1966), and in cases where the coordination is not octahedral, as in the Ca and Sr DPP complexes (following two papers) and the seven-coordinate $Ho(DPP)_3(H_2O)$ (Zalkin, Templeton and Karraker, 1969).

The octahedral complex $Ni(HAA)_2(H_2O)_2(ClO_4)_2$ (Anzenhofer and Hewitt, 1971), in which all the ligands on the Ni^{++} are neutral, does not show this distortion. The distances in Anzenhofer's structure are 2.07, 2.02, 2.04 Å and 2.04, 2.03, 2.05 Å for the three independent distances around the two different Ni atoms, the distance to the water given last in each trio.

The $Mg(DPP)_2$ complex differs from the other octahedral complexes in that the solvent molecules are <u>cis</u> to one another on the coordination octahedron (Fig. 1). The solvent molecules are all <u>trans</u> to one another in the other monomeric complexes. The <u>cis</u> arrangement is not required by the space group symmetry, which could just as easily accommodate the <u>trans</u> configuration, but, while all the other distorted octahedra could be described as tetragonally distorted, the octahedron in $Mg(DPP)_2(DMF)_2$ cannot.

Bullen explains the distortion of the $Co(AA)_2(H_2O)_2$ octahedron in terms of combination of the available <u>d</u>-orbitals of the Co. The same explanation could hold for

the Ni complex as well, but not for the magnesium complexes, since the Mg has no available d-orbitals. Morosin concludes in his paper that the effect is due to packing forces rather than electronic ones since the diaquo Mg complex shows the same distortion as the Co and Ni complexes. The appearance of the same effect in $Mg(DPP)_2(DMF)_2$ and in other structures noted above, where the packing and coordination environments are radically different, as well as the absence of any effect in the octahedral nickel acetylacetone perchlorate complex, leads us to suspect that the effect is primarily electrostatic in origin, with secondary contributions from d-orbital hybridization and packing.

We thank Mrs. Helena Ruben for her advice and assistance concerning many details of this work.

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Table 1. F_o, $\sigma(F_o)$ and final differences for $Mg(DPP)_2(DMF)_2$ (x 10.0). Entries marked with an * were given zero weight in least-squares.

(Table in two parts to be reproduced photographically.)

OBSERVED STRUCTURE FACTORS, STANDARD DEVIATIONS, AND DIFFERENCES (X10.0) FOR
AG(DPPE)2 - ZONE F(0,0,0) = 6592
SG = ESTIMATED STANDARD DEVIATION OF FOB. DEL = /FOB/-/FCA/. * INDICATES ZERO WEIGHTED DATA.

```
 L FOB SG DEL   L FOB SG DEL   L FOB SG DEL   L FOB SG DEL   L FOB SG DEL   L FOB SG DEL   L FOB SG DEL   L FOB SG DEL    L FOB SG DEL   L FOB SG DEL   L FOB SG DEL   L FOB SG DEL   L FOB SG DEL
  H,K= 0, 0     -3 347 11 20    2 363 13 -26    9 101  9 -3   11  56  6 -1  -11  96  6 -10   5 168  6 -6   -6 144  5  7    -9  63  4 15   -4  20 27 -3*  -8  35 14  3    0  28 12 26  -11 142  9 -1
 2 969 18 -71   -2  43 14 -4    4 134  7 -26   10  57  8  3   12  27 29 16*  -10 129  5 -6   6 100  9  3   -5  17 26 13*   -8  61  4 -1   -3  20 27 12*  -7  69  7 -2    1  30 12 -0  -10 105  9  2
 4 881 27-130   -1 987 36 12    6 123  4  1   11   0 26 -14*  13  37 12  5   -9  84  5 -14   7  38 11  6   -4 290  9  6    -7 960 11 14   -2  51  8  1   -6 109  4 -4    2  34 12 15   -9   4 24 -4*
 6  15 21 11*    0  77  8 10    8 260  8 -14    H,K= 2, 12     H,K= 3, 9   -8  91  7 -8   8  97  8 -6   -3 279  9  9    -6 180  6 13   -1  24 38 19*  -5  28 15 -0    3  43  6 12   -8 210  7  2
 8 340 12 -27    1 727 22 -22  10 132 12  6  -10  16 22  0*  -14  40 10 -9  -7  38 19 -4   9  40 41 5*  -2 107  6 12    -5 176  6 14    0  94  5 -8   -4  26 17 -25   H,K= 10, 0    -7 123  5  1
10 291 12 -12    2 116 18 -21  12  35 59 -1*   -9  19 28 11*  -13  27 40 -10*  -6  98  4 -8  10  68 11 -6   -1   0 18 -8*   -4 280  9 26    H,K= 8, 0     -3  60  7 -2  -18  36 11 -3   -6 109  7  6
12 151  7 -9    3 728 22 -93  14  47 11 10   -8  21 29 9*-12    0 27 -22*  -5  46  5 -5  11  42  9  5    0  97  6  4    -3 612 19 56  -18  68  7  8   -2  69  9 -9  -16  58  6  9   -5 316 10  6
14  22 26 -13*   4 509 15 -42   H,K= 2, 2    -7  28 41 -2*-11   0 30 -14*  -4   0 20 -7*  12  67  6 13   1  39  6 10    -2 728 22 77  -16 151 11 -9   -1  97  5 -11 -14 116  5 -5   -4  45  6  5
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OBSERVED STRUCTURE FACTORS FOR MG(OPP)2 - 20MP

(CONTINUED)
PAGE 2

L	FOB	SG	DEL
0	81	8	-11
1	70	6	4
2	38	52	12*
3	41	14	-2
4	0	26	-11*
5	9	30	-5*
6	23	29	20*
7	37	38	-0*
H,K= 12, 4			
-17	19	23	-6*
-16	0	29	-31*
-15	29	30	-2*
-14	0	30	-16*
-13	0	25	-8*
-12	0	30	-1*
-11	0	42	-39*
-10	30	16	20
-9	0	29	-6*
-8	112	5	-2
-7	200	7	-17
-6	28	20	-13*
-5	244	8	-12
-4	109	5	1
-3	146	6	-11
-2	191	6	-1
-1	47	11	-13
0	0	30	-30*
1	25	26	1*
2	96	6	-10
3	57	9	-7
4	55	11	5
5	30	15	-16
6	25	17	13
H,K= 12, 6			
-16	19	38	-17*
-15	71	7	-2
-14	13	25	-24*
-13	0	42	-12*
-12	50	10	8
-11	11	25	6*
-10	31	12	6
-9	20	30	6*
-8	90	16	4
-7	9	30	-3*
-6	191	6	-6
-5	143	5	3
-4	277	9	-14
-3	123	9	-3
-2	133	5	-7
-1	87	6	9
0	90	11	-15
1	84	9	5
2	98	32	-9
3	37	41	23*
4	0	25	-6*
5	28	12	8
H,K= 12, 8			
-14	44	9	6
-13	26	25	-21*
-12	65	6	-6
-11	75	7	-8
-10	57	6	-0
-9	77	9	-2
-8	50	7	-6
-7	19	25	9*
-6	147	9	-5
-5	20	25	6*
-4	148	6	-6
-3	28	15	1
-2	80	4	10
-1	121	5	-11
0	34	10	25
1	35	9	15
2	0	28	-26*
3	0	24	-22*
H,K= 12, 10			
-11	49	8	-13
-10	47	8	-2
-9	66	7	-3
-8	30	11	10
-7	59	5	3
-6	0	24	-27*
-5	0	40	-11*
-4	45	7	3
-3	43	7	3
-2	26	13	22
-1	28	11	9
0	0	26	-10*
H,K= 13, 1			
-18	29	9	28
-17	0	24	-2*
-16	0	29	-4*
-15	38	9	-6
-14	49	11	-3
-13	37	16	-2
-12	117	6	-5
-11	44	29	6
-10	76	12	-1
-9	69	21	-12
-8	134	7	-0
-7	190	7	-19
-6	0	28	-14*
-5	106	8	12
-4	71	6	-1
-3	119	5	-7
-2	16	29	14*
-1	0	41	-28*
0	34	14	-1
1	47	11	-0
2	86	5	-9
3	104	5	7
4	95	5	-1
5	25	24	3
6	31	15	-8
H,K= 13, 3			
-17	27	47	12*
-16	39	8	7
-15	22	24	14*
-14	59	6	3
-13	36	17	16
-12	0	30	-11*
-11	95	6	5
-10	71	7	-3
-9	44	10	-10
-8	90	10	2
-7	128	9	-2
-6	102	5	-4
-5	91	6	4
-4	98	6	1
-3	73	7	1
-2	142	5	-1
-1	30	15	9
0	19	30	6*
1	31	12	18
2	97	6	1
3	49	11	-8
4	24	41	19*
5	60	7	2
H,K= 13, 5			
-16	0	27	-10*
-15	38	13	4
-14	73	5	6
-13	45	12	3
-12	0	30	-11*
-11	6	25	-16*
-10	0	30	-24*
-9	105	6	-4
-8	53	20	-4
-7	82	6	8
-6	57	9	2
-5	72	7	2
-4	87	11	-7
-3	4	30	-37*
-2	69	8	3
-1	22	26	-8*
0	102	10	-9
1	131	5	-6
2	33	19	26
3	53	9	6
4	13	20	-23*
H,K= 13, 7			
-15	49	8	10
-14	27	28	-8*
-13	28	29	12*
-12	89	5	-1
-11	39	14	-10
-10	38	19	-9
-9	27	25	-4*
-8	11	24	1*
-7	0	30	-14*
-6	19	30	-18*
-5	114	6	1
-4	102	9	-1
-3	55	6	-1
-2	23	26	16*
-1	91	5	-5
0	30	12	16
1	0	25	-18*
2	82	5	-5
3	26	13	-3
H,K= 13, 9			
-12	80	9	-1
-11	28	26	1
-10	13	28	-2*
-9	44	11	13
-8	0	29	-23*
-7	22	41	17*
-6	89	4	3
-5	29	12	11
-4	18	49	9*
-3	14	28	11*
-2	19	24	-13*
-1	19	23	-9*
0	16	26	13*
H,K= 14, 0			
-16	45	11	-1
-14	66	8	6
-12	99	5	-6
-10	165	6	4
-8	219	7	-1
-6	177	7	16
-4	29	17	12
-2	0	42	-23*
0	0	28	-6*
2	100	6	-2
4	69	6	8
H,K= 14, 2			
-17	10	27	10*
-16	46	6	9
-15	18	30	5*
-14	109	9	3
-13	69	8	-0
-12	49	11	-8
-11	0	30	-19*
-10	105	6	3
-9	0	27	-14*
-8	34	42	-10*
-7	34	18	5
-6	0	30	-19*
-5	114	5	0
-4	0	30	-30*
-3	0	27	-8*
-2	21	30	8*
-1	68	8	16
0	87	12	-8
1	60	4	-5
2	24	25	7*
3	27	29	-13*
4	0	24	-8*
H,K= 14, 4			
-16	45	9	2
-15	61	15	-1
-14	74	7	11
-13	142	6	8
-12	66	29	-14
-11	214	7	1
-10	93	10	-2
-9	143	8	1
-8	100	5	1
-7	123	5	-2
-6	83	12	-8
-5	71	7	2
-4	62	8	-17
-3	151	5	1
-2	154	6	-1
-1	31	25	-2
0	73	7	-4
1	51	6	18
2	29	29	0*
3	55	6	2
4	26	27	17
H,K= 14, 6			
-15	39	7	18
-14	83	5	-1
-13	44	7	7
-12	114	6	0
-11	44	8	9
-10	204	7	2
-9	76	7	-9
-8	209	7	-2
-7	44	13	-14
-6	161	6	-4
-5	13	29	-0*
-4	94	10	3
-3	65	8	-8
-2	71	7	6
-1	97	9	6
0	22	25	-2*
1	40	8	3
2	21	27	9*
H,K= 14, 8			
-12	17	27	-8*
-11	49	6	4
-10	93	8	-4
-9	60	16	-2
-8	40	8	7
-7	94	5	-1
-6	29	12	13
-5	37	9	5
-4	0	29	-25*
-3	0	40	-10*
-2	48	9	9
-1	42	6	18
0	26	11	13
H,K= 15, 1			
-17	44	20	-0
-16	90	19	14
-15	35	9	22
-14	39	14	-17
-13	73	7	-4
-12	78	7	-0
-11	73	5	-7
-10	85	5	-4
-9	152	5	2
-8	0	42	-9*
-7	99	5	4
-6	73	7	2
-5	18	30	-9*
-4	32	14	-22
-3	39	15	-6
-2	68	6	-13
-1	23	30	9*
0	89	6	-5
1	79	6	7
2	46	10	20
3	10	27	4*
H,K= 15, 3			
-16	37	12	-1
-15	0	28	-29*
-14	99	6	-0
-13	0	30	-15*
-12	110	5	6
-11	98	6	-2
-10	106	6	1
-9	108	5	3
-8	108	10	-8
-7	68	31	2
-6	32	23	-7
-5	38	15	7
-4	193	8	8
-3	24	29	16*
-2	114	6	-6
-1	67	11	11
0	30	23	19
1	18	29	-13*
2	20	28	4*
H,K= 15, 5			
-15	88	4	4
-14	93	17	1
-13	111	9	-9
-12	63	6	-2
-11	89	11	10
-10	0	30	-14*
-9	9	42	-14*
-8	20	26	-23*
-7	97	7	-6
-6	24	30	20*
-5	5	42	-3*
-4	15	42	15*
-3	20	25	-5*
-2	0	25	-15*
-1	87	6	11
0	16	39	-6*
1	41	10	7
H,K= 15, 7			
-13	12	26	6*
-12	42	10	3
-11	20	28	-4*
-10	101	5	-10
-9	15	29	14*
-8	51	7	0
-7	49	7	-9
-6	26	29	-0*
-5	58	8	7
-4	30	11	12
-3	17	28	7*
-2	16	27	14*
-1	0	37	-8*
H,K= 16, 0			
-16	76	6	1
-14	54	6	2
-12	29	10	8*
-10	135	6	4
-8	131	5	3
-6	33	43	-24*
-4	61	9	6
-2	0	30	-14*
0	95	9	-3
H,K= 16, 2			
-16	42	6	9
-15	66	7	1
-14	19	28	6*
-13	116	5	2
-12	100	6	-2
-11	78	9	13
-10	65	14	10
-9	12	30	-13*
-8	13	29	-3*
-7	133	6	2
-6	5	30	-15*
-5	42	14	0
-4	39	9	20
-3	34	42	-6*
-2	60	8	-3
-1	74	9	-3
0	53	17	2
1	55	7	0
H,K= 16, 4			
-15	0	37	-7*
-14	109	5	1
-13	24	28	1*
-12	76	6	5
-11	73	24	12*
-10	90	6	-6
-9	38	14	24
-8	54	6	-1
-7	58	15	-2
-6	35	42	10*
-5	106	5	6
-4	101	5	-1
-3	89	5	-3
-2	46	10	1
-1	90	6	-1
0	15	37	-2*
H,K= 16, 6			
-13	12	26	9*
-12	40	11	-3
-11	23	28	14*
-10	51	19	4
-9	0	28	-30*
-8	56	8	6
-7	3	29	-29*
-6	119	5	3
-5	37	9	2
-4	87	6	1
-3	33	9	17
-2	68	6	7
H,K= 17, 1			
-15	32	9	-3
-14	0	23	-12*
-13	49	7	-1
-12	36	9	21
-11	92	5	4
-10	84	6	3
-9	169	6	3
-8	116	5	-1
-7	76	13	4
-6	131	6	-6
-5	0	29	-34*
-4	56	9	-8
-3	60	5	9
-2	2	24	1*
-1	77	6	-2
H,K= 17, 3			
-14	110	5	-1
-13	38	17	0
-12	121	5	1
-11	93	9	18
-10	71	7	11
-9	13	29	7*
-8	21	24	9*
-7	74	7	1
-6	101	5	2
-5	38	14	5
-4	95	4	-1
-3	35	39	20*
-2	60	5	1
H,K= 17, 5			
-12	0	37	-11*
-11	27	27	-8*
-10	0	23	-8*
-9	81	6	4
-8	42	8	-4
-7	71	6	3
-6	77	6	-1
-5	40	8	-8
-4	37	16	6
-1	99	5	13
H,K= 18, 0			
-12	71	9	0
-10	89	10	-1
-8	12	28	-18*
-6	10	24	-1*
-4	0	27	-5*
H,K= 18, 2			
-13	52	15	-4
-12	67	5	-2
-11	0	23	-10*
-10	21	28	6*
-9	89	9	4
-8	19	26	16*
-7	98	6	-0
-6	0	35	-7*
-5	10	23	-1*
-4	59	7	7
H,K= 18, 4			
-10	50	6	-2
-9	66	9	24
-8	38	8	-2
-7	37	10	7
-6	76	4	-1

Table 2. Final coordinates and thermal parameters. Standard deviations of the least significant digit(s) are given in parentheses. The form of the temperature factor ($\underline{B}$ in units of $\mathring{A}^2$) is $\underline{T} = \exp(-0.25(\underline{B}_{11}\underline{h}^2\underline{a}^{*2} + 2\underline{B}_{12}\underline{hka}^*\underline{b}^* + \cdots))$ for anisotropic, and $\underline{T} = \exp(-\underline{B}\sin^2\theta/\lambda^2)$ for isotropic thermal parameters.

(Table to be reproduced photographically.)

ATOM	X	Y	Z	B11	B22	B33	B12	B13	B23
MG	0	.3373(1)	.250	3.68(8)	3.44(8)	4.85(9)	0	2.14(7)	0
O(1)	-.0439(2)	.4524(2)	.1553(2)	3.8(1)	4.1(1)	5.3(1)	-.14(9)	2.0(1)	.5(1)
O(2)	.1176(1)	.3437(2)	.2419(2)	4.0(1)	3.3(1)	5.7(1)	.08(9)	2.6(1)	.3(1)
C(01)	-.0231(3)	.6479(3)	.0215(3)	5.1(2)	4.5(2)	4.8(2)	.3(2)	2.3(2)	-.1(2)
C(02)	-.0672(3)	.7344(4)	-.0270(3)	6.9(3)	5.4(2)	4.7(2)	-.2(2)	2.3(2)	.8(2)
C(03)	-.1258(3)	.7868(4)	-.0060(4)	6.2(3)	5.2(2)	6.4(3)	.9(2)	2.0(2)	1.4(2)
C(04)	-.1402(3)	.7543(4)	.0634(3)	4.7(2)	5.2(2)	7.1(3)	1.4(2)	2.4(2)	.6(2)
C(05)	-.1006(2)	.6647(3)	.1085(3)	4.3(2)	5.2(2)	5.1(2)	.5(2)	2.2(2)	.7(2)
C(06)	-.0398(2)	.6115(3)	.0890(2)	3.6(2)	4.0(2)	4.2(2)	-.2(1)	1.5(1)	.0(1)
C(07)	.0047(2)	.5173(3)	.1419(2)	4.1(2)	3.9(2)	4.1(2)	-.1(1)	1.9(1)	-.3(1)
C(08)	.0974(2)	.5087(3)	.1741(3)	3.7(2)	3.5(2)	5.5(2)	-.1(1)	2.3(2)	.4(2)
C(09)	.1479(2)	.4250(3)	.2216(2)	4.2(2)	3.5(2)	4.9(2)	.1(1)	2.7(2)	-.5(1)
C(10)	.2463(2)	.4253(3)	.2503(2)	3.6(2)	3.7(2)	4.4(2)	.1(1)	2.0(1)	-.1(1)
C(11)	.2917(3)	.3328(3)	.2601(3)	4.3(2)	4.2(2)	6.4(2)	.1(2)	2.4(2)	-.5(2)
C(12)	.3813(3)	.3321(5)	.2873(3)	5.0(2)	6.3(3)	7.5(3)	2.2(2)	3.0(2)	.6(2)
C(13)	.4285(3)	.4226(5)	.3074(3)	3.6(2)	9.2(4)	6.8(3)	.5(2)	2.4(2)	1.0(2)
C(14)	.3860(3)	.5152(5)	.3003(3)	4.3(2)	6.2(3)	7.8(3)	-1.0(2)	2.0(2)	1.0(2)
C(15)	.2956(3)	.5167(4)	.2719(3)	4.4(2)	4.2(2)	7.1(3)	.1(2)	2.0(2)	.5(2)
O(3)	.0579(2)	.2222(2)	.3473(2)	4.5(1)	4.3(1)	5.5(1)	.7(1)	2.4(1)	1.0(1)
C(16)	.1330(3)	.1852(3)	.3767(3)	5.1(2)	5.5(2)	4.9(2)	1.0(2)	2.5(2)	.7(2)
N(1)	.1725(2)	.1250(3)	.4443(2)	5.6(2)	5.4(2)	4.6(2)	1.5(1)	1.6(1)	.8(1)
C(17)	.1281(4)	.0975(5)	.4965(4)	11.1(4)	10.5(4)	9.5(4)	3.2(3)	5.9(3)	4.9(3)
C(18)	.2608(6)	.082(1)	.4699(7)	7.3(4)	11.3(7)	10.4(6)	4.5(5)	3.0(4)	3.3(5)
H(C1)	.016(3)	.615(3)	.008(2)	5.1(10)					
H(02)	-.057(2)	.754(3)	-.075(3)	6.5(11)					
H(03)	-.153(3)	.838(4)	-.044(3)	7.8(13)					
H(04)	-.187(4)	.788(4)	.069(3)	9.5(15)					
H(05)	-.109(2)	.641(3)	.161(2)	5.1(9)					
H(06)	.127(2)	.560(3)	.158(2)	4.7(9)					
H(07)	.258(2)	.275(3)	.238(2)	4.8(9)					
H(08)	.406(3)	.272(4)	.290(3)	7.9(14)					
H(09)	.491(3)	.427(3)	.331(3)	7.1(11)					
H(10)	.416(3)	.573(3)	.314(3)	5.7(11)					
H(11)	.264(2)	.573(3)	.267(2)	4.3(9)					
H(12)	.162(3)	.197(3)	.347(3)	5.6(11)					
H(13)	.291(4)	.100(5)	.533(5)	11.8(23)					
H(14)	.251(4)	.021(5)	.462(5)	9.4(25)					
H(15)	.298(5)	.125(6)	.449(5)	13.9(28)					
H(16)	.181	.095	.573	12.000					
H(17)	.078	.140	.487	12.000					
H(18)	.1088	.0205	.4882	12.000					

Table 3. Bond angles (deg) around magnesium[a]

Atom(1) -Mg-	Atom(2)	Angle
O(1)	O(1)[b]	87.9
O(1)	O(3)	174.0
O(1)	O(3)[b]	91.3
O(2)	O(1)	86.3
O(2)	O(1)[b]	90.4
O(2)	O(2)[b]	175.4
O(2)	O(3)	87.8
O(2)	O(3)[b]	95.5
O(3)	O(3)[b]	90.2

(a) Standard deviation of each angle is ±0.1°.

(b) Related by two-fold axis through Mg.

Table 4. Intra-molecular and intra-complex distances (Å)[a]

Atoms		Distance	Atoms		Distance
C(01)	C(02)	1.381(6)	C(01)	H(01)	0.90(4)
C(02)	C(03)	1.372(7)	C(02)	H(02)	0.94(4)
C(03)	C(04)	1.369(7)	C(03)	H(03)	0.88(5)
C(04)	C(05)	1.376(6)	C(04)	H(04)	0.94(5)
C(05)	C(06)	1.393(5)	C(05)	H(05)	1.01(4)
C(06)	C(01)	1.377(5)	C(08)	H(06)	0.94(4)
C(06)	C(07)	1.489(5)	C(11)	H(07)	0.90(4)
C(07)	O(1)	1.261(4)	C(12)	H(08)	0.87(5)
C(07)	C(08)	1.408(5)	C(13)	H(09)	0.95(5)
C(08)	C(09)	1.381(5)	C(14)	H(10)	0.87(4)
C(09)	O(2)	1.277(4)	C(15)	H(11)	0.88(3)
C(09)	C(10)	1.504(5)	C(16)	H(12)	0.86(4)
C(10)	C(11)	1.384(5)	C(17)	H(16)[c]	1.19
C(11)	C(12)	1.367(6)	C(17)	H(17)[c]	0.96
C(12)	C(13)	1.363(7)	C(17)	H(18)[c]	1.03
C(13)	C(14)	1.366(7)	C(18)	H(13)	0.98(6)
C(14)	C(15)	1.377(6)	C(18)	H(14)	0.79(6)
C(15)	C(10)	1.389(5)	C(18)	H(15)	1.02(8)
O(3)	C(16)	1.228(5)			
C(16)	N(1)	1.288(5)	Mg	O(1)	2.057(3)
N(1)	C(17)	1.441(6)	Mg	O(2)	2.055(2)
N(1)	C(18)	1.461(7)	Mg	O(3)	2.095(3)
O(1)	O(1)[b]	2.855(5)	O(2)	O(3)	2.878(3)
O(1)	O(2)	2.811(3)	O(2)	O(3)[b]	3.072(3)
O(1)	O(2)[b]	2.917(3)	O(3)	O(3)[b]	2.968(5)
O(1)	O(3)[b]	2.967(3)			

(a) Standard deviations given in parentheses.

(b) Related by two-fold axis through Mg.

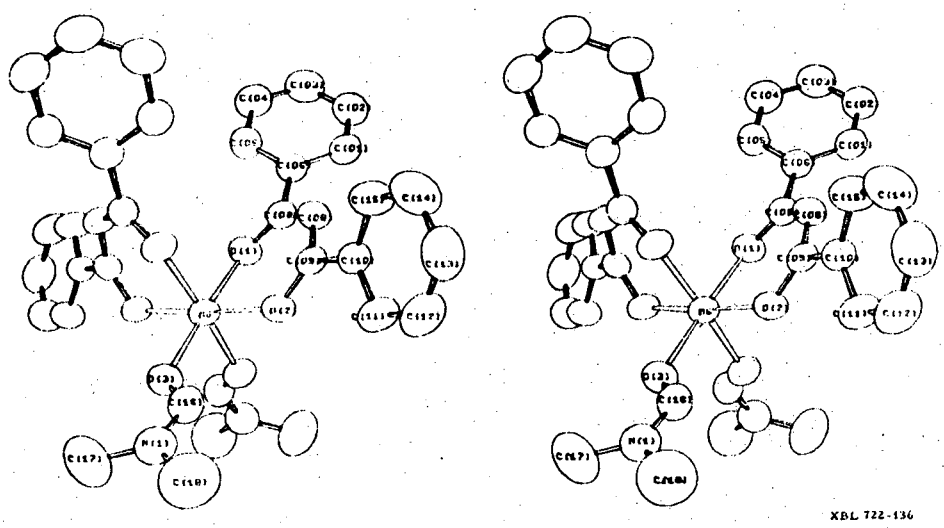
(c) Positions not refined by least-squares.

Figure Captions

Fig. 1. Stereoscopic view of the complex, showing configuration and labeling. The two-fold crystallographic axis runs vertically in the plane of the drawing. Hydrogens have been omitted for clarity. Thermal ellipsoids are scaled to include 50% probability.

Fig. 2. Oxygen coordination of the Mg, showing distortion of the octahedron. The projection is down the two-fold axis onto the ac plane.

Fig. 3. Stereoscopic view of the unit cell, showing packing of complexes. Labeled axes are positive from the origin. Hydrogens have been omitted for clarity.



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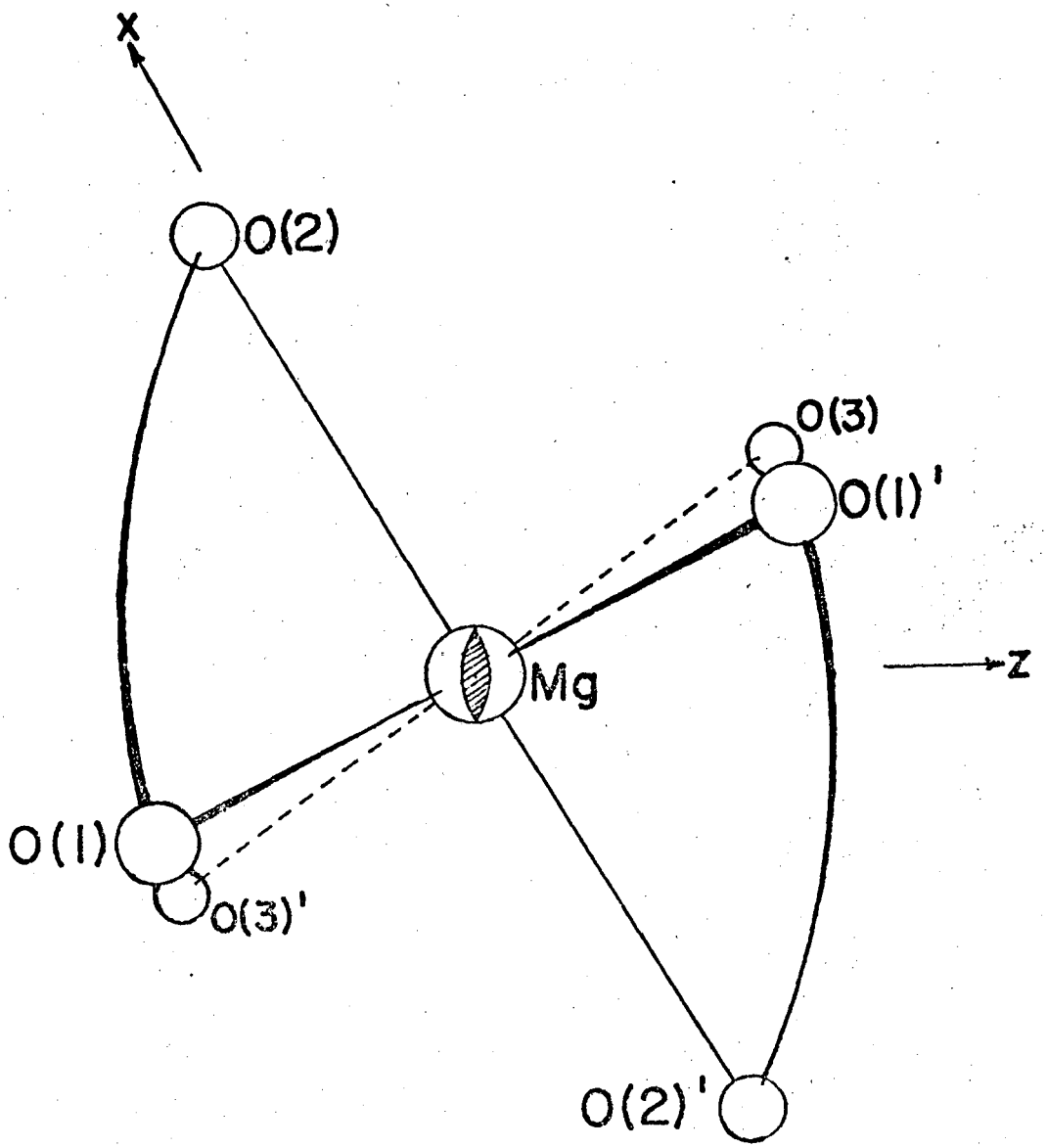

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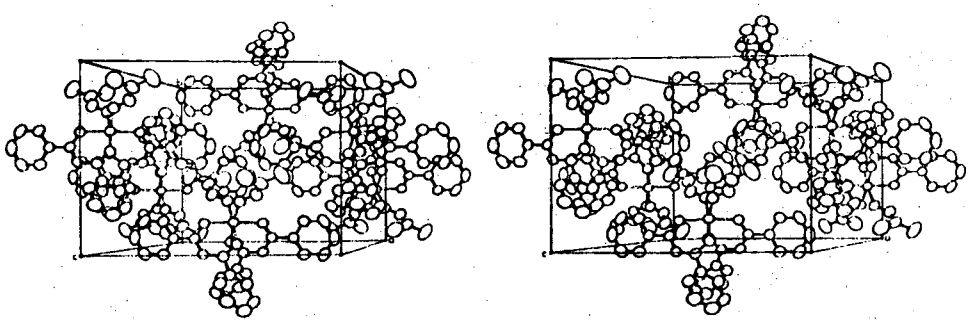

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TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720