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TRIETHYLMETHYLAMMONIUM BIS(PENTAMETHYLCYCLOPENTADIENYL)-MANGANATE(-1): THE FIRST STRUCTURAL CHARACTERIZATION OF AN ANIONIC METALLOCENE

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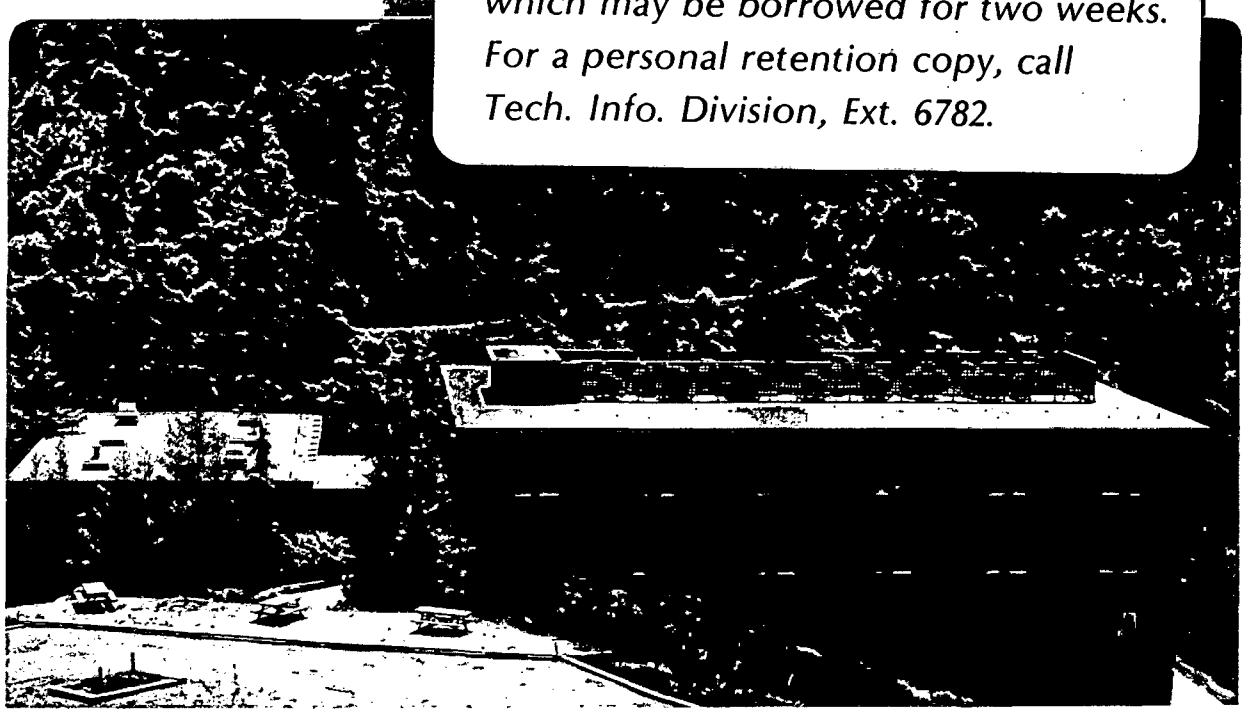

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Triethylmethylammonium Bis(pentamethylcyclopentadienyl)manganate(-1): The First Structural Characterization of an Anionic Metallocene

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Abstract

The structural characterization of the first metallocene anion is reported. The salt triethylmethylammonium bis(pentamethylcyclopentadienyl)-manganate(-1) contains well separated ions with no unusual interactions. The anion shows a regular metallocene structure like the isoelectronic ferrocene except the conformation of the rings is eclipsed, with a resultant D_{5h} point symmetry for the metallocene anion. The average Mn-C bond length, 2.066(2) Å, is slightly longer than expected from comparisons with the isoelectronic ferrocene and cobalticinium metallocenes. This is ascribed as one of the results of the extraordinary electron pressure of the anion. The space group is $P2_1/n$ (an alternate setting of $P2_1/c$) with a = 14.54(6), b = 18.954(7), c = 9.612(3) Å, β = 99.11(4)° and Z = 4. For 1579 independent amplitudes used in the refinement of 262 variables, R = 4.4, R_w = 4.3%.

Introduction

A high level of interest in the structure and bonding in sandwich type complexes has continued since the discovery of ferrocene.[1] This has resulted in the formulation of a general picture of first row transition metal sandwich compounds which may be used to rationalize trends in their behavior. Indeed, many observed structural trends are especially well accommodated by current qualitative bonding arguments.[2-5] However, resolution of structural subtleties in cyclopentadienyl complexes by room temperature X-ray methods has been hampered by the low barrier to ring rotation. In contrast, use of permethylated analogs has substantiated structural fine points which are difficult to obtain in the unsubstituted species.[6] As part of a study of the structural characteristics of the permethylated metallocene complexes we have determined the structure of the novel decamethylmanganocene anion as the triethylmethylammonium salt.

The anomalous properties of manganocene and several of its alkylated derivatives are well documented[2,7,8] and make this series of sandwich compounds a unique one. Interest in the molecular structure of decamethylmanganocene anion is essentially twofold. This 18 electron sandwich is to serve as a benchmark or model compound for the possible identification of Jahn-Teller distortions in orbitally degenerate permethylmetallocenes of the first row transition series. Additionally, the decamethylmanganocene anion is the first anionic metallocene to be isolated and structurally characterized, and its electron richness has been well documented.[8,9] The effect of this electron richness and anionic character on the molecular structure is of interest. In this

light a comparison with the isoelectronic Fe(II) and Co(III) analogs is made; the structure of the permethylmanganocene anion shows differences which are consistent with an extraordinarily electron-rich metallocene.

Experimental

The title compound was prepared by the metathesis of the Na^+ salt.[9] Crystals were mounted in a dry box under inert atompshere in quartz capillary tubes, sealed with grease, and flame sealed promptly on removal from the dry box. Of several crystals examined, an irregularly shaped fragment gave the best single crystal diffraction pattern with peaks of acceptable mosaic spread. Intensity data were collected using MoK_α radiation (λ = .71073 Å) on an Enraf-Nonius CAD-4 diffractometer. All instrumentation and computational methods used have been previously described.[10] Preliminary cell dimensions were determined from 24 reflections found by a low angle search. A monoclinic cell was indicated by preliminary precession photos. The systematic absences (0k0, k odd; and h0ℓ, h+ℓ = odd) define the space group as $P2_1/n$. Cell constants determined using 22 reflections with $2\theta > 20°$ are given in Table I along with the other selected crystal and experimental data. Other parameters relevant to the data collection are similar to those previously reported for MoK_α radiation[4] with the exceptions being noted.

All intensity data were reduced to F_o^2 and $\sigma(F_o^2)$ with corrections for variable scan speed, Lorentz, and polarization effects only.[10] Full-matrix least-squares refinement[11] minimizing the function $\Sigma w(|F_o| - |F_c|)^2$ was employed using independent reflections with $F_o^2 > 3\sigma(F_o^2)$. The final agreement factors are R = 4.4%, R_w = 4.3%, and

GOF = 1.779 where n_o = 1579, n_v = 262.[12] Final values of the positional parameters for the non-hydrogen atoms are given in Table II. Information regarding supplementary materials may be found in the last paragraph of this paper.

The structure was solved by standard Patterson and least-squares/difference Fourier techniques. All hydrogens were placed at calculated positions (C-H = .95 Å, tetrahedral angles) assigned B_{iso} = 10.0 $Å^2$ and were not refined. The methyl hydrogens on the C_5Me_5 ligands were positioned in a staggered orientation with respect to the Mn-C_r vector. This orientation has been observed in other η^5-C_5Me_5 moieties,[4-6,13] and is consistent with the electron density maps of this structure. The largest peak in the final difference Fourier is less than twice the background level, and peaks above background do not substantiate any disorder or omissions in the model employed.

Results and Discussion

The geometry of the anion and a packing diagram for $[(Me)(Et)_3N][(C_5Me_5)_2Mn]$ are shown in Figures 1 and 2, respectively. The anions and cations display no unusually short interactions, which minimizes the role of interionic steric effects in governing the anion structure. The alkyl ammonium cation exhibits the expected structure, with an average N-C distance of 1.493(5) Å and an average C-C distance of 1.52(3) Å and is not of further interest here. Selected bond lengths for the permethylmanganocene anion are presented in Table III using the numbering scheme given in Figure 1. The average Mn-C_r distance of 2.066(2) Å is larger than that found for other d^6 metallocenes,[3-5]

however, this distance is still closer to the typical R(M-C) for d^6 metallocenes than for metallocenes with an electron imbalance of one. The C_5Me_5 ligands are symmetrically coordinated (i.e. no ring slippage) and the C-C bond distances are typical of the corresponding distances in other η^5-C_5Me_5 moieties.[4,5,13] No bond localization is substantiated in the C_5 rings. As is also normal for permethylmetallocenes, the C_5 rings in the decamethylmanganocene anion are planar and parallel (dihedral angle of .4°) with the methyl carbon atoms bent out of the C_5 plane — away from the metal. This movement is pronounced for the title compound in comparison to other permethylmetallocenes.[4,5] Thus the decamethylmanganocene anion shows many features which are characteristic of a d^6 metallocene and further confirms the general picture of an undistorted metallocene [i.e. a monomeric sandwich type structure with planar, parallel, and symmetrically coordinated C_5 rings at an appropriate $\bar{R}$(M-C)].

However, a comparison with other permethylmetallocenes studied by us[4,5] shows that the permethylmanganocene anion exhibits two unusual structural features which seem to be intimately related. An examination of the $\bar{R}$(M-C)'s for the isoelectronic permethylmetallocenes where M = Mn(I), Fe(II), and Co(III) shows that the $\bar{R}$(M-C) for Mn(I) is larger than that found for Fe(II) and Co(III) at a greater than 99% confidence interval. This increase in $\bar{R}$(M-C) for Mn(I) is not solely explained by the differing formal charge on the metal, since the Fe(II) and Co(III) analogs gave identical $\bar{R}$(M-C)'s [2.050(2) Å];[4,5] but may be rationalized by the increased steric interactions between opposing rings for the Mn(I) metallocene, caused by the second unusual feature of the

anion — it's near D_{5h} symmetry. In contrast to all other decamethylmetallocenes studied by us,[4,5] the permethylmanganocene anion adopts an eclipsed ring conformation and not a staggered one. This suggests that the increase in steric strain between opposing C_5Me_5 rings in going from a staggered to an eclipsed configuration is relatively small. The magnitude of this steric effect is supported by the observed disorder found for the decamethylferrocenium cation in two solid state structures[14] and the low barrier found for ring rotation in gas phase decamethylferrocene (1 kcal/mole).[15] Thus, the underlying cause for the eclipsed ring configuration observed in this work is not clear, but involves only a very small energy difference. Comparison of the interionic contacts for the title compound and $[Co(C_5Me_5)_2][PF_6]$[4] and the intermolecular contacts of $Fe(C_5Me_5)_2$[5] does not indicate that the D_{5h} symmetry of the permethylmanganocene anion is obviously determined by packing forces. Use of electronic arguments to explain the anomalous symmetry of the title compound is also discouraged by comparison again with the isoelectronic Fe(II) and Co(III) analogs.

In summary, the bis(pentamethylcyclopentadienyl)manganate(-1) anion is the first structurally characterized metallocene anion. The general structural features show a strong similarity with the isoelectronic 18 electron metallocene cobalt cation or ferrocene itself. There is a small increase in the average Mn-C bond length which is ascribed to the extraordinary electron density of this metallocene and, most remarkably, the structure is fixed in the solid state as the eclipsed D_{5h} structure.

Acknowledgment

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Supplementary Material

Supplementary material includes anisotropic thermal parameters for all non-hydrogen atoms, positional parameters for all hydrogen atoms, distances of selected atoms to the least squares plan of the C_5 ring, and a listing of F_o and F_c. Ordering information is given on current masthead page.

References

1. Kealy, T. J.; Pauson, P. L. Nature 1951, 168, 1039.

2. Almenningen, A.; Haaland, A.; Samdal, S. J. Organomet. Chem. 1978, 149, 219.

3. Haaland, A. Acc. Chem. Res. 1979, 12, 415.

4. Gilbert, B. P.; Hollander, F. J.; Robbins, J. L.; Raymond, K. N., submitted for publication.

5. Freyberg, D. P.; Robbins, J. L.; Raymond, K. N.; Smart, J. C. J. Am. Chem. Soc. 1979, 101, 892

6. Byers, L. R.; Dahl, L. R. Inorg. Chem. 1980, 19, 277.

7. Ammeter, J. H. J. Magn. Res. 1978, 30, 299. Switzer, M. E.; Wang, R.; Rettig, M. F.; Maki, A. H. J. Am. Chem. Soc. 1974, 96, 7669. Ammeter, J. H.; Bucher, R.; Oswald, N. J. Am. Chem. Soc. 1974, 96, 7833.

8. Robbins, J. L.; Edelstein, N. M.; Cooper, S. R.; Smart, J. C. J. Am. Chem. Soc. 1979, 101, 3853. Smart, J. C.; Robbins, J. L. J. Am. Chem. Soc. 1978, 100, 3936.

9. Robbins, J. L. Ph.D. Dissertation, University of California, Berkeley, California, 1981.

10. Eigenbrot, C. W., Jr.; Raymond, K. N. Inorg. Chem. 1982, 21, 2653.

11. Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Vol. IV; The Knoch Press, Birmingham, England, 1974; Table 2.2B. Cromer, D. T., ibid., Table 2.3.1.

12. $R = \frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|}$ $\qquad R_w = \left\{\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma w F_o^{\,2}}\right\}^{1/2}$

$$GOF = \left\{\frac{\Sigma w(|F_o| - |F_c|)^2}{(n_o - n_v)}\right\}^{1/2}$$

where n_o is the number of observations, n_v the number of variable parameters, and the weights, w, were given by

$$w = \frac{4F_o^{\,2}}{\sigma^2(F_o^{\,2})}, \quad \sigma^2(F_o^{\,2}) = \left\{\sigma_o^{\,2}(F_o^{\,2}) + (pF^2)^2\right\}$$

where p (0.02 for this structure) is the factor used to lower the weight of intense reflections.

13. Teller, R. G.; Williams, J. K. Inorg. Chem. 1980, 19, 2770. Churchill, M. R.; Ni, S. W. J. Am. Chem. Soc. 1973, 95, 2150.

14. Miller, J. S.; Reis, A. H.; Gebert, E.; Ritsko, J. J.; Salaneck, W. R.; Kovnat, L.; Cape, T. W.; Van Duyne, R. P. J. Am. Chem. Soc. 1979, 101, 7111. Reis, A. H.; Preston, L. D.; Williams, J. M.; Peterson, S. W.; Candela, G. A.; Swarzendruber, L. J.; Miller, J. S.; Rice, M. J. J. Am. Chem. Soc. 1979, 101, 2765.

15. Almenningen, A.; Haaland, A.; Samdal, S.; Brunvoll, J.; Robbins, J. L.; Smart, J. C. J. Organomet. Chem. 1979, 173, 293.

Table I. Crystal and Data Collection Parameters

Formula	$MnNC_{27}H_{48}$
Molecular weight (g/mol)	441.63
Cell constants[a]	
a (Å)	14.541(6)
b (Å)	18.954(7)
c (Å)	9.612(3)
β (°)	99.11(4)
Cell volume ($Å^3$)	2616(3)
Formula units per cell	4
Space group[b]	$P2_1/n$
Calculated density (g/cm^3)	1.12
Absorption coefficient MoK_α, μ (cm^{-1})	5.4
2θ Limit (°)	45
hkℓ Collected	+h ±k ±ℓ
Scan angle (°)	.55 + .35 tanθ
Total number of reflections	3780
Independent reflections	1579

[a]Based on the setting angles of 24 reflections at an ambient temperature of 23°C.

[b]An alternate setting of $P2_1/c$. Symmetry operations are ±(x,y,z); ±(1/2 + x, 1/2 - y, 1/2 + z).

Table II. Positional parameters for non-hydrogen atoms.

Atom	x	y	z
Mn	0.25215(8)	0.05331(5)	0.2445(1)
N	0.1712(3)	-0.1893(3)	-0.4255(5)
C1	0.2077(4)	-0.0490(3)	0.2126(5)
C2	0.1449(4)	-0.0117(3)	0.2815(6)
C3	0.1937(4)	0.0136(3)	0.4113(6)
C4	0.2884(4)	-0.0087(3)	0.4221(6)
C5	0.2982(4)	-0.0476(3)	0.2985(5)
C6	0.2474(5)	0.1625(3)	0.2507(7)
C7	0.3398(4)	0.1397(3)	0.2600(6)
C8	0.3476(4)	0.1012(3)	0.1378(6)
C9	0.2583(4)	0.0987(3)	0.0512(5)
C10	0.1962(4)	0.1373(3)	0.1239(6)
C11	0.1805(4)	-0.0901(4)	0.0764(7)
C12	0.0396(4)	-0.0035(4)	0.2320(7)
C13	0.1525(4)	0.0539(4)	0.5218(6)
C14	0.3642(4)	0.0036(4)	0.5464(6)
C15	0.3834(4)	-0.0866(3)	0.2694(7)
C16	0.2093(5)	0.2092(4)	0.3543(8)
C17	0.4192(5)	0.1581(4)	0.3767(7)
C18	0.4362(5)	0.0697(4)	0.0977(7)
C19	0.2349(6)	0.0686(4)	-0.0935(6)
C20	0.0954(5)	0.1537(4)	0.0642(8)
C21	0.2112(5)	-0.1391(4)	-0.3137(8)
C22	0.3033(6)	-0.1645(5)	-0.2266(9)
C23	0.0830(5)	-0.1557(4)	-0.4941(8)
C24	0.1569(5)	-0.2625(4)	-0.3711(8)
C25	0.2356(6)	-0.1967(5)	-0.5311(8)
C26	0.0275(6)	-0.1998(5)	-0.6145(8)
C27	0.0937(6)	-0.2661(5)	-0.2667(9)

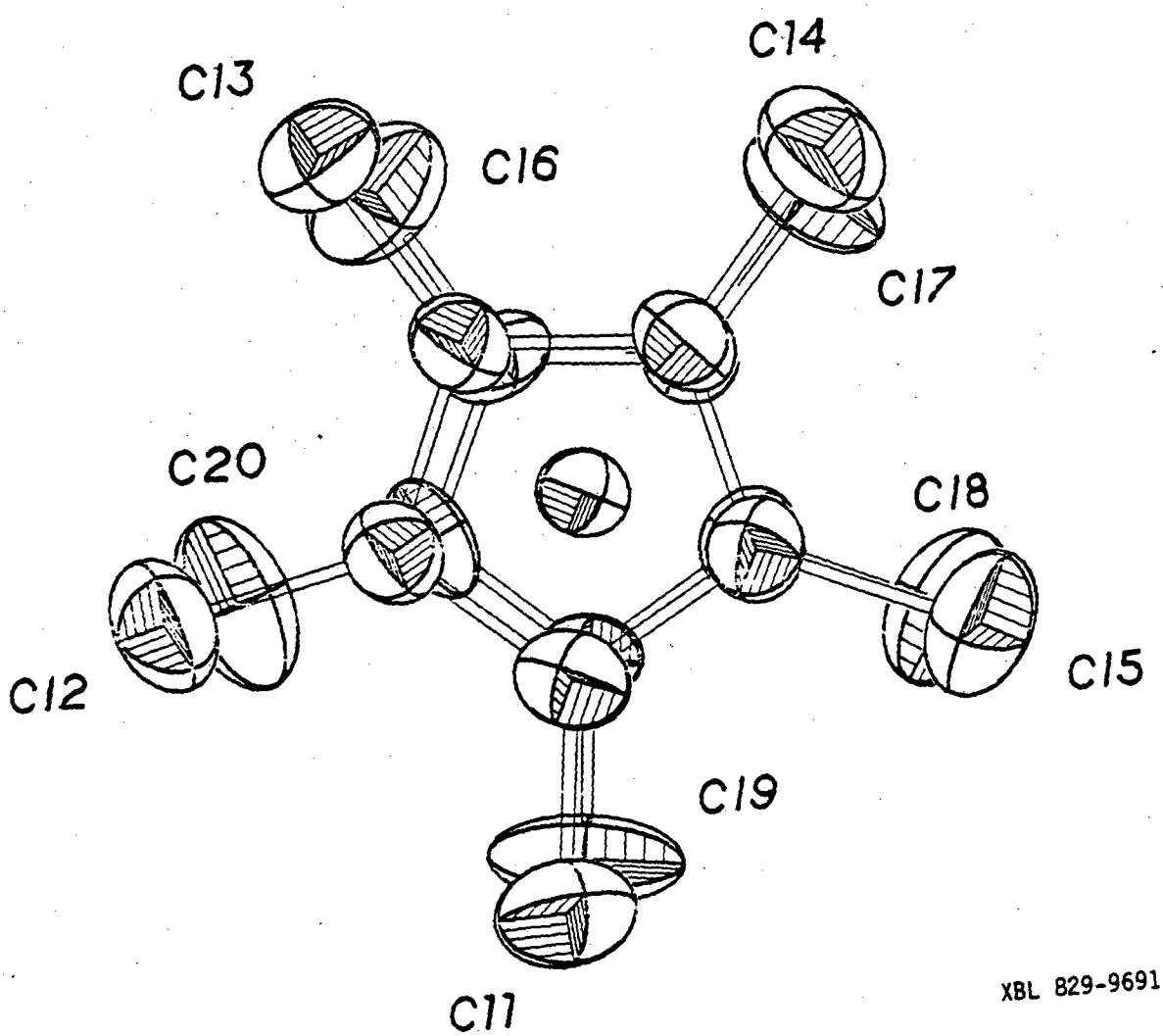
Table III. Selected Interatomic Distances for the Decamethylmanganocene Anion.

Ring I		Ring II	
Atoms	Distance (Å)	Atoms	Distance (Å)
Mn - C1	2.066(6)	Mn - C6	2.072(4)
- C2	2.062(5)	- C7	2.065(5)
- C3	2.071(5)	- C8	2.061(5)
- C4	2.071(5)	- C9	2.062(5)
- C5	2.066(6)	- C10	2.059(5)
Av.	2.067(2)	Av.	2.064(2)
C1 - C2	1.409(7)	C6 - C7	1.401(7)
C2 - C3	1.418(6)	C7 - C8	1.402(6)
C3 - C4	1.428(6)	C8 - C9	1.427(6)
C4 - C5	1.424(6)	C9 - C10	1.427(6)
C5 - C1	1.439(5)	C10 - C6	1.407(7)
Av.	1.424(5)	Av.	1.413(6)
C1 - C11	1.514(7)	C6 - C16	1.502(7)
C2 - C12	1.537(6)	C7 - C17	1.518(6)
C3 - C13	1.506(6)	C8 - C18	1.524(6)
C4 - C14	1.510(6)	C9 - C19	1.507(6)
C5 - C15	1.506(7)	C10 - C20	1.520(7)
Av.	1.515(6)	Av.	1.514(4)

Figure Captions

Figure 1. An ORTEP drawing of a decamethylmanganocene anion. Thermal ellipsoids are drawn at the 50% probability contour. Ring carbon atoms are numbered ten less than the adjacent methyl carbon atom.

Figure 2. A packing diagram for $[(C_2H_5)_3(CH_3)N][Mn(C_5Me_5)_2]$ viewed down the c axis. The b axis is vertical.



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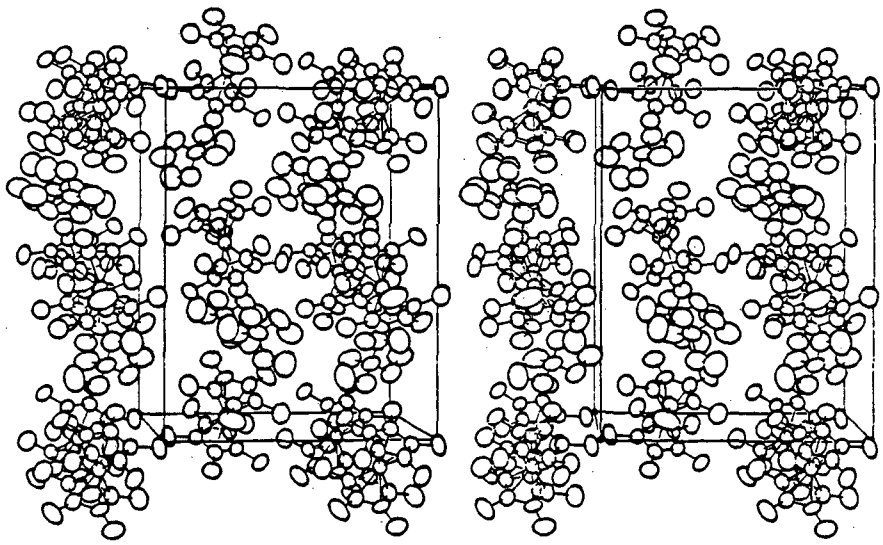

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