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The Crystal Structure of the Complex of Hexamethylenetetramine with Manganous Chloride*

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Single crystals of the complex of hexamethylenetetramine with manganous chloride were grown in a 1:1 mixture of alcohol and acetone. By chemical analysis the composition was shown to correspond to the formula $MnCl_2.2(CH_2)_6N_4.2H_2O$. The structure has a pseudo unit cell with $a_1 = 11{\cdot}80$, $a_2 = 22{\cdot}00$ and $a_3 = 7{\cdot}21$ Å, which contains four molecules. A few weak reflections require that the a_1 axis be doubled; these apparently arise from a slight collapse of the pseudo structure. Since the determination of the pseudo structure leads to a satisfactory understanding of the nature of the complex, we have considered it unprofitable to investigate the exact nature of the collapse, and have neglected the weak reflections throughout. The space group when the weak reflections are neglected is C_{2v}^9–$P2_1nb$.

A trial structure derived from steric considerations and the intensities of reflections $h00$ led to a satisfactory interpretation of the Patterson distribution function. The structure based on the Patterson syntheses was confirmed by the Fourier projection $\rho(y, z)$, and by calculation of structure factors for reflections $h00$ and $0kl$.

The structure has the following important features. The complex molecule is shown by the parameter values to have a center of symmetry at the manganese atom, which lies on the common three-fold axis of the two hexamethylenetetramine molecules. The Mn–Cl bonds are approximately normal to the Mn–N bonds. Both the Patterson syntheses and the Fourier projection $\rho(y, z)$ indicate that two molecules of water are present in each complex molecule, and the Mn–O bonds are approximately normal to the plane of the Mn–Cl and Mn–N bonds. The bonds about the manganese atom are thus approximately octahedrally directed. Lengths of the central bonds are Mn–Cl = 2·47, Mn–N = 2·40 and Mn–O = 2·00 Å.

1. Introduction

From water or organic solvents HMT† precipitates in crystalline complexes with a suprisingly large number of inorganic compounds. We have investigated by X-ray diffraction crystals of one of these HMT complex compounds, $MnCl_2.2(CH_2)_6N_4.2H_2O$, which may be representative of a great many others. A structure has emerged which explains the stability of the complex compound.

2. Preparation and characterization

Preparation of crystals

Anhydrous c.p. manganous chloride and c.p. HMT were separately dissolved in 1:1 mixtures of alcohol and acetone. The solutions were mixed, and the fine crystals which precipitated were allowed to grow for periods of a few days to a few weeks in a relatively very large volume of mother liquor.

The solvents were respectively of absolute and c.p. grades, and for some preparations were further dried over alumina. Nonetheless, the crystals always contained water of crystallization. The large volume of solvent and slow growth make it not surprising that the necessary small amount of water could have been picked up, provided that the crystal structure bonds the water strongly, for example to manganese.

Chemical analysis and formula

A crop of carefully grown small crystals was dried by centrifuging and over silica gel to constant weight. About 100 mg. of hand-picked crystals were subjected to microchemical analysis for manganese, chlorine, carbon, nitrogen and hydrogen. The results are given in the first three columns of Table 1. A large error in the analytical result for hydrogen is to be expected; the general agreement is satisfactory. The ratio of $MnCl_2$ to $(CH_2)_6N_4$ is 1:2. The analytical indication of

Table 1. *Analysis*

			No. of atoms in the pseudo unit	
Element	Found (%)	Calculated* (%)	From analysis, density and cell volume	For 4 molecules*
Mn	12·25	12·40	4·04	4
Cl	16·07	16·03	8·10	8
C	32·84	32·60	48·40	48
N	25·06	25·35	31·80	32
H	3·58	6·40	63·60	112
O	(10·20)	(7·22)		8
	100·00	100·00		

* For the formula $MnCl_2.2(CH_2)_6N_4.2H_2O$.

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* Contribution No. 1465 from the Gates and Crellin Laboratories.

† HMT stands for *hexamethylenetetramine* throughout this paper.

water of crystallization accords with several independent types of observations reported later, such as the weight of a unit cell.

We therefore take as the formula for the complex molecule $MnCl_2.2(CH_2)_6N_4.2H_2O$.

Morphological and physical properties of the crystal

Acetone favors acicular growth of the crystal along the a_3 axis, and alcohol favors a habit tabular on (100). Goniometric measurement and assignment of indices to faces as shown in Fig. 1 gave

$$a_1 : a_2 : a_3 = 0{\cdot}530 : 1{\cdot}000 : 0{\cdot}325.$$

The morphology indicated the absence of a center of symmetry.

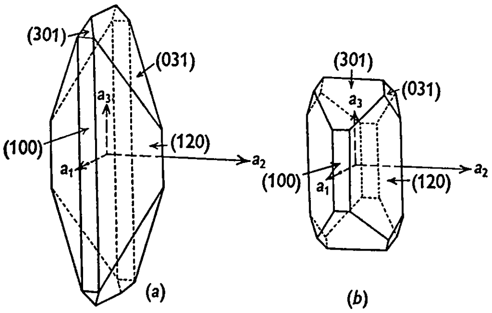

Fig. 1. (*a*) Crystals prepared from a 1 : 1 mixture of alcohol and acetone; (*b*) crystals from a 1·4 : 1 mixture.

The crystals gave a fairly strong piezo-electric effect,* which confirms the absence of a center of symmetry.

The magnetic susceptibility of the compound was determined with a Gouy magnetic balance at room temperature and at 40·5° C.† On the basis of the formula $MnCl_2.2(CH_2)_6N_4.2H_2O$ each manganese atom has 5·17 unpaired electrons.

The density of the crystals, as determined by displacement, is $1{\cdot}570 \pm 0{\cdot}01$ g.cm.$^{-3}$.

X-ray powder diffraction patterns were used to confirm the identity of successive preparations.

3. The unit cell and space group

Laue photographs were taken with continuous radiation, minimum wave-length 0·29 Å, of two crystals mounted along two different axes. They confirmed orthorhombic symmetry.

Rotation photographs around each of the three axes a_1, a_2 and a_3 were taken in a camera of diameter 100 mm. with copper K radiation filtered through nickel foil 0·025 mm. thick. From measurements of equatorial reflections the three axial lengths are

$$a_1 = 11{\cdot}80 \pm 0{\cdot}01, \quad a_2 = 22{\cdot}00 \pm 0{\cdot}02$$

and $$a_3 = 7{\cdot}21 \pm 0{\cdot}01 \text{ Å};$$

and the axial ratio is

$$a_1 : a_2 : a_3 = 0{\cdot}536 : 1{\cdot}000 : 0{\cdot}328.$$

This unit cell has the volume 1874 ± 6 Å^3 and contains four molecules. On the basis of the formula

$$MnCl_2.2(CH_2)_6N_4.2H_2O,$$

the X-ray density is 1·567 g.cm.$^{-3}$. Conversely, from the analytical data, observed density and cell volume, we calculate the fourth column of Table 1.

In indexing the Weissenberg photographs (see below) for the zero and first levels along a_2 and a_3 we found some extremely weak reflections which indicate that the a_1 axis of length 11·80 Å is only a pseudo axis, and that the true identity distance in this direction is $A_1 = 2a_1 = 23{\cdot}60$ Å. Reflections which corroborate this doubling of a_1 were then found to be present but extremely weak on the rotation photograph about a_1. We have, nonetheless, found it profitable to base our investigation upon the pseudo unit cell. Indices *hkl* throughout this paper therefore refer to the pseudo unit, and not to the true unit.

Equi-inclination Weissenberg photographs were taken with filtered copper K radiation in a camera of diameter 57·30 mm. which moved 0·5 mm. per degree of crystal rotation. To facilitate eventual intensity measurements, quadruple Eastman No-Screen films were used, and equant crystals with dimensions 0·1–0·15 mm. were selected. The layer lines were recorded for h from zero through six, k from zero through thirteen, and l from zero through four. Each layer line showed maxima out to $\sin\theta/\lambda = 0{\cdot}930$. We obtained 1286 reflections for one octant of the reciprocal lattice. Among these, 68 are not on the reciprocal lattice of the pseudo unit.

The systematic extinctions were established on the Weissenberg photographs with numerous missing reflections to support them. Neglecting the weak reflections which contradict the pseudo unit, and accepting earlier evidence that the crystal belongs to the orthorhombic hemihedry, we determined the space group to be C_{2v}^{9}–$P2_1nb$.*

On the basis of the true unit cell, considering all reflections, we observe: (1) reflections Hkl for all values of H, k and l; (2) reflections $0kl$ for all values of k, l and $k+l$; (3) reflections $Hk0$ only for H and k even; (4) reflections $H0l$ only for H even; and (5) reflections $00l$ only for l even. Then C_s^2–$P11b$ is the space group or a subgroup for the true unit cell.

The continuation with the approximation based on the pseudo unit cell can be justified in many ways. Since on the two Weissenberg photographs with $k=0$ and $l=0$, respectively, reflections with H odd are too weak to be detected, neither of the corresponding two-dimensional projections will show any minor features

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* We are indebted to Prof. W. N. Lipscomb for testing our crystals by the method of Giebe & Scheibe (cf. Wooster, 1938, p. 207).

† We are indebted to Mr David L. Douglas for assistance in the magnetic determination.

* If one overlooks the piezoelectric test, the possible centrosymmetric space group is D_{2h}^{16}–$Pmnb$. It would require the four manganese atoms to take one of three sets of special positions. Each set, however, can be eliminated by reference to the Patterson function or by stereochemical considerations.

which do not repeat according to a_1. Reflections with H odd contribute all together only 1 % to the sum of the corrected intensities, and the strongest one among them has a value of 20 for the structure factor (with $F_{000}=1624$). Although the exact structure is undoubtedly based on the larger unit cell, the difference between the exact and pseudo structures is not significant for this investigation.

4. The collection and reduction of intensity data

The intensity data were drawn from the Weissenberg photographs already described, by application of the visual method improved by Shoemaker (1947). The film factor was taken as 3·7.

The estimated intensities were divided by polarization and Lorentz factors, but extinction and absorption were neglected. We determined an absolute scale factor by the method of Wilson (1942). We included all of the 1218 reflections which were actually observed from the pseudo reciprocal lattice, but assigned only zero intensity to each of those which were not observed. Further, the anhydrous formula was used in calculating the values of Σf_i^2. The square of the absolute value of the structure factor based on the absolute scale could therefore be too low, but probably never too high.

5. The search for a trial structure

A trial structure was derived from the chemical composition of the compound, the space group, the intensities of a few remarkably strong reflections, the known structure of the HMT molecule, steric considerations and a few reasonable assumptions.

(1) *The orientation of the HMT molecules in the crystal*

For 600, the strongest reflection, $|F|$ on an absolute scale is equal to or greater than 275. Since the sum of the f values of all manganese, chlorine and oxygen atoms is only 182, the carbon and nitrogen atoms must contribute strongly. We assume throughout this work that the HMT group has essentially the same structure as in crystalline HMT.* Calculation of F_{600} for all possible orientations of the group indicates that the carbon and nitrogen atoms will contribute enough to F_{600} when, and only when, one of the four three-fold axes of each HMT molecule approximately lines up along a_1. In this case the HMT molecules contribute about 150 to F_{600}. The carbon and nitrogen atoms as well as the manganese, chlorine, and even oxygen atoms must distribute themselves in the neighborhood of a set of planes which, with proper choice of origin, have $x=0, \frac{1}{6}, \frac{1}{3}, \frac{1}{2}, \frac{2}{3}$ and $\frac{5}{6}$. It is remarkable that the apex and the base of a HMT molecule are separated by a distance of about 2 Å, which closely approximates $\frac{1}{6}d_{100}$.

(2) *The symmetry of the complex molecule*

Each complex molecule must lie in a general position and be equivalent to every other. The knowledge of the HMT structure reduces the number of parameters to twenty-seven.

The formula suggests that some sort of two-fold symmetry element may pass through the central manganese atom. We were unable to reconcile a rotation axis or mirror plane with the Patterson distribution. A center of symmetry was assumed; this assumption led to an acceptable structure determination.

(3) *The relative positions along a_1 of the two HMT molecules in a single complex molecule*

Fig. 2 shows the five possible arrangements in an asymmetric quadrant of the unit cell of two nonequivalent HMT molecules, HMT I and HMT II, with reference to the x co-ordinates only.

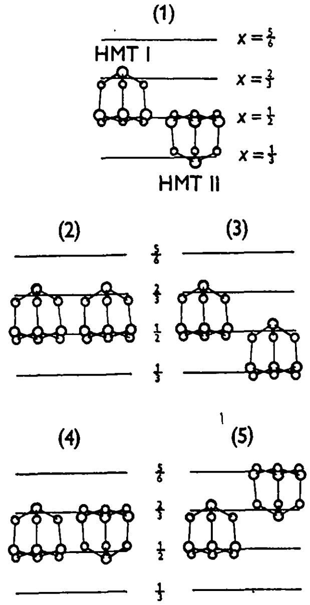

Fig. 2. The five possible arrangements of the two nonequivalent HMT molecules in an asymmetric quadrant of the unit cell, with reference to the x co-ordinates and direction only.

The assumption of a center of symmetry in the complex molecule excludes the arrangements (2) and (3). Owing to the fact that the manganese atom at the center of a complex molecule must be on one of the set of planes with $x=0, \frac{1}{6}, \frac{1}{3}, \frac{1}{2}, \frac{2}{3}$ and $\frac{5}{6}$, and that F_{400} is equal to or greater than 180, the arrangement in Fig. 2 (1) is the only appropriate one, and HMT I and HMT II belong to one complex molecule.

(4) *The location of the manganese atom and the center of the HMT molecules, with reference to the y, z co-ordinates only*

With the arrangement (1) the carbon and nitrogen atoms of the bases of the two HMT molecules are dis-

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* The molecule has symmetry T_d–$43m$ (Dickinson & Raymond, 1923). The shortest C–N and N–N distances are 1·45 and 2·42 Å respectively (Shaffer, 1947).

tributed in the neighborhood of the plane $x=\frac{1}{2}$. The base of a molecule as outlined by van der Waals radii is dimensioned in Fig. 3. A trial of alternatives in the plane $x=\frac{1}{2}$ shows that bases should not make contact at nitrogen atoms if reasonable positions are to be available for manganese atoms. Instead the effective radius of a base must be 3·3 Å. Consideration of the a_2 glide finally locates the bases in the yz plane as shown in Fig. 4. The assumption of central symmetry for the complex molecule places the manganese atoms.

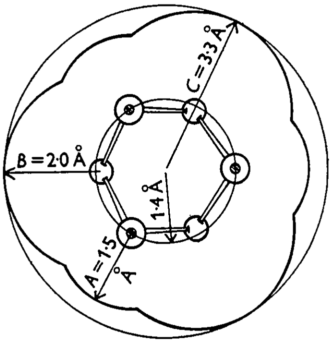

Fig. 3. The effective radius of the base of a HMT molecule. The van der Waals radius of a nitrogen atom is represented by A; the van der Waals radius of a methyl group by B; and the effective radius of the base by C (Pauling, 1940).

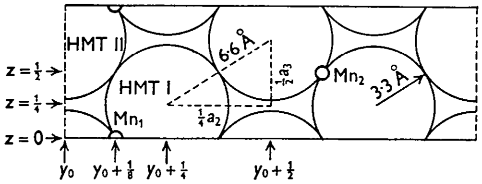

Fig. 4. The confinement by steric considerations of the manganese atoms and the centers of the bases of the HMT molecules, with respect to their y, z co-ordinates. Owing to the coincidence of $\sqrt{\{(\frac{1}{4}a_2)^2+(\frac{1}{2}a_3)^2\}}$ with the effective diameter of the base of a HMT molecule, which is 6·6 Å, the centers must be located as shown in the figure.

The y co-ordinates of the symmetry elements remain, however, undetermined. The approximate co-ordinates of the four manganese atoms in the unit can be given as below:

Mn_1	$(\frac{1}{2}, y_0+\frac{1}{8}, 0)$	Mn_2	$(\frac{1}{2}, y_0+\frac{5}{8}, \frac{1}{2})$
Mn_3	$(0, \frac{3}{8}-y_0, \frac{1}{2})$	Mn_4	$(0, \frac{7}{8}-y_0, 0)$

The x co-ordinates follow rigorously from the space group. The z co-ordinates inherit the uncertainties in the above derivation.

(5) *The x co-ordinates of the chlorine atoms*

No space remains at $x=0$ or $\frac{1}{2}$. Because of the center of symmetry in the complex molecule and because of the two-fold screw axis, two chlorines lie in each of the planes $x=\pm\frac{1}{6}, \frac{1}{3}, \frac{2}{3}$. The designations and levels of the two chlorines which are co-ordinated with Mn_1 are

$$Cl_{1-I} \text{ at } x=\tfrac{2}{3} \quad \text{and} \quad Cl_{1-II} \text{ at } x=\tfrac{1}{3}.$$

6. The determination of the pseudo structure

(1) *The application of the Patterson synthesis*

We classify manganese and chlorine as heavy atoms, and carbon, nitrogen and oxygen as light. It was fully recognized at the beginning, and borne out by experience, that Patterson projections at best can resolve only peaks arising from interactions between heavy atoms, while suitable Patterson sections can show some recognizable interactions between a heavy atom and a light atom. Thus per unit cell of the three-dimensional Patterson function the possibly distinguishable peaks, aside from that at the origin, are as follows:

Class	Kind of interaction responsible for the peak	No. of theoretically distinct peaks
1	Harker, heavy atom–heavy atom	9
	Non-Harker, heavy atom–heavy atom*	10
2	Non-Harker, heavy atom–light atom	264

* The number is reduced from twelve by the center of symmetry of the complex molecule. A corresponding correction has not been applied to the number of peaks of class 2.

The Patterson summations and later Fourier summations were carried out by means of the L cards on International Business Machines (Shaffer, Schomaker & Pauling, 1946).

(*a*) *Determination of the co-ordinates of the heavy atoms in the crystal by the Patterson synthesis.* The Patterson projections $P(v,w)$ and $P(u,v)$ are presented in Figs. 5 and 6 respectively. The identification and interpretation of the heavy peaks of class 1 on both projections were carried out in the following manner. The approximate co-ordinates for the manganese atoms derived for the trial structure lead one to expect outstanding Harker peaks due to Mn–Mn interactions as given below.

Peak	Symmetry element	Interactions	Positions
1	$2_1 \parallel a_1$	Mn_1–Mn_4, Mn_2–Mn_3	$(\frac{1}{2}, 2y_0+\frac{1}{4}, 0)$
2	a_2 glide $\perp a_3$	Mn_1–Mn_2, Mn_3–Mn_4	$(0, \frac{1}{2}, \frac{1}{2})$
3	n glide $\perp a_2$	Mn_1–Mn_3, Mn_2–Mn_4	$(\frac{1}{2}, 2y_0-\frac{1}{4}, \frac{1}{2})$

In the Patterson projection $P(v,w)$ one will find peak 1 in the neighborhood of the line $w=0$. However, three peaks were found in that neighborhood. If the peak at $(\frac{1}{8}, 0)$ on the projection $P(v,w)$ were the peak 1, then peak 3 would appear near $(\frac{3}{8}, \frac{1}{2})$ on the same figure, and peak 1 would appear near $(\frac{1}{2}, \frac{1}{8})$ on the projection $P(u,v)$. If the peak at $(\frac{3}{8}, 0)$ on $P(v,w)$ were the peak 1, then peak 3 would appear in the neighborhood of $(\frac{1}{2}, \frac{1}{8})$ on the projection $P(u,v)$. By elimination one thus identifies unambiguously as peak 1 the peak at (0·240, 0) on the projection $P(v,w)$. Then y_0 is −0·005.

With knowledge of the x co-ordinates of the manganese and chlorine atoms one identifies two peaks due to the interactions Mn–Cl within each complex molecule; they are the heavy peak near $(\frac{1}{6}, 0)$ on $P(u,v)$, and that near $(0, \frac{1}{6})$ on $P(v,w)$. In view of the elongation of both peaks the manganese and chlorine atoms in one complex molecule would be expected not to have the same y co-ordinates. To confirm the identification of Mn–Cl peaks we made the Patterson section $P(u, 0, w)$ (Fig. 7).

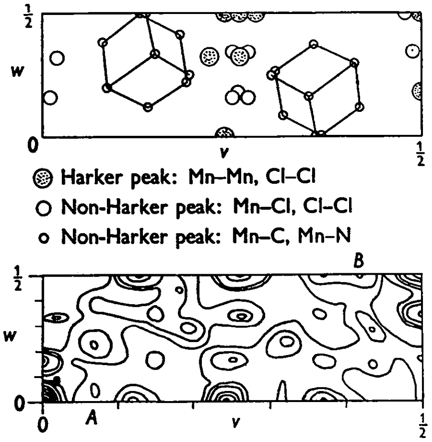

Fig. 5. The Patterson projection $P(v, w)$ with the theoretica map for the interatomic vectors between the heavy atoms and between manganese and HMT. The contour line intervals on an arbitrary scale are 900, 1250, 1500, 2000, 2500, 3000, 3500 and 4000.

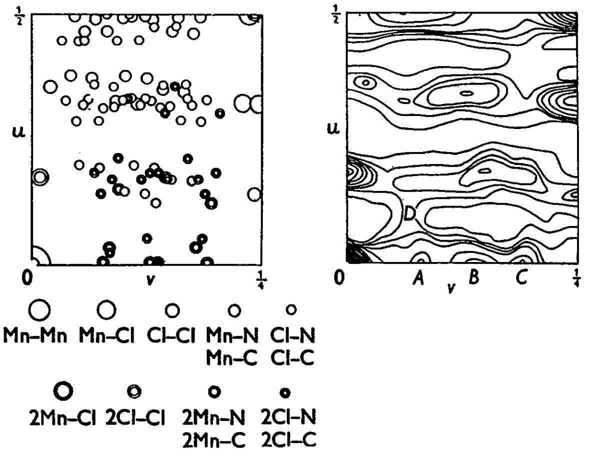

Fig. 6. The Patterson projection $P(u, v)$ with the theoretical map for the interatomic vectors between heavy atoms and between heavy and light atoms. The contour line intervals on an arbitrary scale are −100, 0, 50, 100, 200, ..., 1000, 1200 and 1300.

The co-ordinates of the heavy atoms in the complex molecule 1 are now established, as follows:

Mn_1	(0·500, 0·120, 0)
Cl_{1-I}	(0·683, 0·130, −0·170)
Cl_{1-II}	(0·317, 0·110, 0·170)

On the basis of these values we calculated the heights of the 19 peaks of Class 1 and their positions, and indicate them on the vector maps of Figs. 5 and 6.

(*b*) *Determination of the positions of HMT molecules in the crystal by the Patterson synthesis.* A manganese atom which lies in the plane $x = \frac{1}{2}$ between the centers of two HMT molecules cannot find room between two methylene groups, but will find ample room between two nitrogen atoms, if the two HMT molecules are so arranged that each of them has a nitrogen atom lying on the line connecting their centers. One is now able to see the HMT molecule even on the projection $P(v, w)$ in Fig. 5, and to recognize that the peaks other than A, B, and those of Class 1 are due to the interactions between the manganese atom and the light atoms of a whole HMT molecule. The interactions between the chlorine atoms and the light atoms are not important in this projection, though they may perturb the Mn–C and Mn–N peaks.

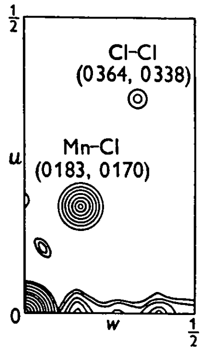

Fig. 7. The Patterson section $P(u, 0, w)$. The contour line intervals on an arbitrary scale are 100, 150, 200, 250, 300, 350, 400, 500, 1000, 1500 and 2000.

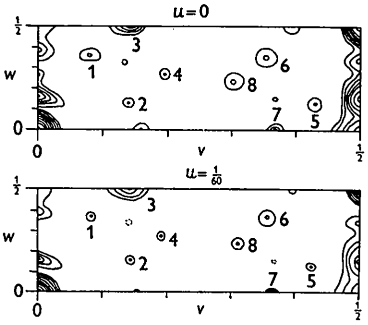

Fig. 8. The Patterson sections $P(0, v, w)$ and $P(\frac{1}{60}, v, w)$. The contour line intervals on an arbitrary scale are 100, 150, 200, 250, 300, 400, 500, 1000, 1500 and 2000.

In the projection $P(u, v)$ in Fig. 6 the peaks A, B and C in the neighborhood of the line $u = 0$ can be due only to the intramolecular interactions of Class 2, and they are fairly well resolved. These peaks, together with the rough arrangement of HMT molecules deduced from Fig. 4 or 5 or earlier, fix the two HMT molecules around one manganese atom.

The three peaks are resolved in the sections $P(0, v, w)$ and $P(\frac{1}{60}, v, w)$ (Fig. 8). The pair of peaks 1 and 2 are due to the Mn–C interactions, the pair 3 and 4 to Mn–N. The distance between the first pair of peaks is essentially the C–C distance found in the HMT molecule.

The N–N distance is reproduced by the pair 3 and 4. This strongly suggests that the respective pairs of atoms have the same x co-ordinates. The distance between the peaks of the pairs 1, 3 and 2, 4 is the C–N distance projected in this plane. Furthermore the peaks 1, 2, 3 and 4 have essentially the same prominence in both sections. On the basis of this evidence we assumed that the pairs of carbon and nitrogen atoms in question are distributed approximately on the levels $x = x_{\mathrm{Mn}} \pm \frac{1}{120}$. The three peaks A, B and C select the combinations $x_{\mathrm{Mn}} - \frac{1}{120}$ and $x_{\mathrm{Mn}} + \frac{1}{120}$ for the pairs of carbon and nitrogen atoms in HMT I, and $x_{\mathrm{Mn}} + \frac{1}{120}$ and $x_{\mathrm{Mn}} - \frac{1}{120}$ for the pairs of carbon and nitrogen atoms in HMT II.

It turns out that the manganese atom lies on the common three-fold axis of the two HMT molecules.

(2) *Projections of the distribution function for electron density; the calculation of structure factors*

(*a*) *The calculation of structure factors for reflections* $h00$. With the x co-ordinates taken from the Patterson synthesis, and neglecting the water, we obtained the values for F_{h00} which are listed in Table 2, column A. The observed values for $|F|$, readjusted by a new scale factor, are included for comparison. For the reflections $h00$,

$$\Sigma \,||F|_o - |F|_c| \div \Sigma |F|_o = 11{\cdot}2\,\%.$$

Table 2. F_{h00} *values*

$h00$	$\|F\|_o$	F_c	
		A	B
000	—	748	812
200	212	207	212
400	169	143	122
600	320	292	283
800	47	57	67
10.0.0	120	94	102
12.0.0	80	88	85

(*b*) *The Fourier projection* $\rho(y, z)$ *and the calculation of structure factors for reflections* $0kl$. Using the parameters obtained in the previous section we calculated the signs of the structure factors for about 75 reflections $0kl$ which occur at the lower Bragg angles and were not too weak. A Fourier summation gave back peaks for all atoms approximately at the positions we had assumed. While the projection does not refine the parameters of the light atoms, a new set of values for the y, z parameters of the manganese and chlorine atoms was determined. The new co-ordinates turned out to be finally acceptable and appear in Table 4. With these new values for the heavy atoms and with light atom parameters revised on the basis of the new manganese parameters we calculated structure factors for all observed reflections $0kl$, 109 in number, and carried out another Fourier summation which is plotted as $\rho(y, z)$ in Fig. 9. Comparison of the projection with Fig. 10 confirms the approximate structure in a convincing fashion.

The crowding of the atoms in this projection and the disparity in their atomic numbers create a pattern which at many points is beyond the resolving power of the reflections which could be observed with copper $K\alpha$ radiation and a maximum $\sin\theta$ of 0·93; specifically, carbon and nitrogen atoms separated by less than about 0·2 Å were not resolved. A Fourier projection on (001) may be expected to give better resolution. For the purpose of this work we are, however, satisfied with the projection in Fig. 9, inasmuch as it shows all isolated atoms and groups of superimposed atoms, and they can be recognized readily.

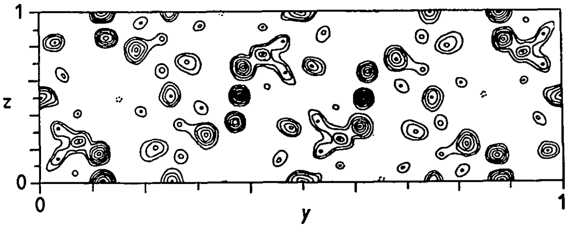

Fig. 9. The Fourier projection $\rho(y, z)$. Contour-line intervals are 7·5, 10, 15, 20, 25, 35 and 45 e.Å^{-2}.

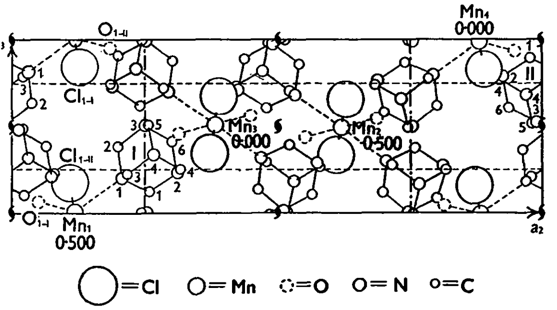

Fig. 10. The pseudo structure of the HMT complex with manganous chloride. One unit cell is shown; the a_1 axis is normal to the plane of the paper and points away from the reader. Hydrogen atoms are not shown.

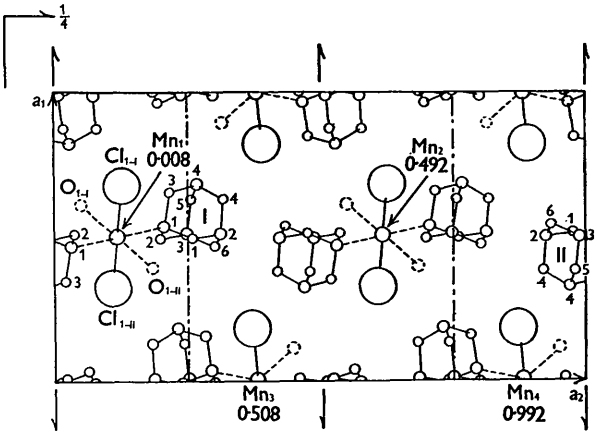

Fig. 11. In this view of the pseudo structure the a_3 axis is normal to the plane of the paper and points away from the reader. Key as for Fig. 10.

The calculated structure factors for the reflections $0kl$ are given as entry A in Table 3 along with the

Table 3. *Observed and calculated structure factors* 0*kl*

a = absent. $F_{000} = 748(A) = 812(B)$

		F_c	
k	$\|F\|_o$	A	B
0*k*0			
2	13	11	16
4	26	5	12
6	34	−73	−63
8	84	160	117
10	52	66	59
12	110	−105	−115
14	89	−81	−94
16	108	84	102
18	43	−24	−21
20	72	−77	−70
22	51	−87	−75
24	37	22	16
26	49	37	36
0*k*1			
1	58	76	112
2	18	−28	−28
3	103	−138	−148
4	120	−75	−93
5	62	−124	−102
6	*a*	0	14
7	34	63	42
8	72	80	76
9	85	106	78
10	*a*	−25	−30
11	32	−47	−46
12	*a*	12	12
13	90	−81	−98
14	*a*	17	9
15	*a*	9	13
16	*a*	12	7
17	52	65	78
18	53	45	49
19	*a*	−10	−10
20	52	−31	−34
21	77	−58	−44
22	*a*	4	8
23	*a*	−24	−23
24	35	33	31
25	38	49	42
0*k*2			
0	54	−42	−2
1	9	9	13
2	*a*	2	1
3	*a*	8	18
4	18	−5	−2
5	50	−7	−28
6	*a*	−10	−2
7	65	52	50
8	130	113	85
9	*a*	−34	−40
10	*a*	4	2
11	11	2	14
12	14	−1	−7
13	18	−40	−28
14	*a*	−20	−30
15	*a*	−13	−28
16	53	53	66
17	58	52	61
18	*a*	25	27
19	*a*	4	3
20	34	14	19
21	47	−40	−45
22	48	−47	−38
0*k*3			
1	75	−55	−42
2	10	4	4
3	8	−14	−22
4	55	10	−24
5	52	−14	−5
6	*a*	10	35
7	12	−9	−17
8	52	−46	−53
9	30	−39	−49
10	8	4	−3
11	10	−8	−5
12	43	−39	−21
13	17	−28	−37
0*k*4			
0	67	54	60
1	15	30	39
2	*a*	−6	−10
3	*a*	2	10
4	6	−9	−9
5	*a*	−1	8
6	*a*	−6	0
7	23	−24	−22
8	20	26	21
9	60	−87	−100
10	24	28	31
11	*a*	2	0
12	37	20	22
13	40	19	34
14	*a*	−16	−18
15	*a*	1	−16
16	50	27	30
17	53	−21	−8
18	*a*	16	14
19	*a*	3	0
20	*a*	−12	−13
21	68	58	49
0*k*5			
1	63	70	66
2	37	−22	−20
3	82	−63	−67
4	24	−20	−43
5	29	−77	−75
6	*a*	−17	0
7	21	−18	−15
8	*a*	12	18
9	48	68	72
10	23	−50	−56
11	23	−40	−36
12	54	49	65
13	72	−44	−43
14	*a*	0	−14
15	*a*	2	2
16	*a*	18	10
17	62	56	54
18	24	−38	−28
19	*a*	−2	−6
20	*a*	−25	30
21	36	−52	−54
0*k*6			
0	132	125	115
1	23	−46	−39
2	*a*	18	14
3	*a*	16	17
4	45	−57	−58
5	*a*	−21	−18
6	*a*	−33	−32
7	70	51	46
8	122	142	149
9	*a*	−56	−60
10	18	5	11
11	*a*	9	9
12	70	73	77

Table 3 (*cont.*)

		F_c	
k	$\lvert F\rvert_o$	A	B
$0k6$			
13	29	56	65
14	41	− 63	− 61
15	*a*	− 22	− 30
16	*a*	38	34
17	37	− 13	− 4
18	*a*	40	35
19	35	− 34	− 35
$0k7$			
1	26	17	8
2	*a*	28	34
3	40	− 68	− 68
4	*a*	− 6	− 11
5	74	− 76	− 75
6	24	22	24
7	40	57	63
$0k7$			
8	*a*	− 18	− 16
9	42	47	56
10	*a*	11	4
11	35	− 26	− 29
13	48	− 55	− 48
14	28	14	13
15	*a*	11	9
16	47	34	35
$0k8$			
0	35	50	37
2	*a*	− 19	− 21
4	31	− 12	− 14
6	*a*	− 8	− 9
8	36	28	40
9	40	17	13

observed $|F|$'s, which have been adjusted by a new and slightly different scale factor such that

$$\Sigma\,|F|_c = \Sigma\,|F|_o.$$

The value for the expression

$$\Sigma\,|\,|F|_o - |F|_c\,| \div \Sigma\,|F|_o$$

is 33 % (absent reflections are neglected).

(3) *The probable positions of the oxygen atoms in the crystal*

Most Patterson projections we made have been almost completely interpreted, and the Fourier projection converged to an extent such that one might expect to find some information regarding the oxygen atoms. In fact we did probably find X-ray evidence concerning them.

In the projection $P(v, w)$ in Fig. 5 the peaks A and B were not explained, nor were the positive values near D in Fig. 6. These features do not correspond to any possible vector between atoms belonging to the anhydrous part of the complex molecules. However, they may be accounted for by putting two oxygen atoms into the complex molecule 1 at the positions

	x	y	z
$O_{1-\mathrm{I}}$	0·610	0·052	0·064
$O_{1-\mathrm{II}}$	0·390	0·186	0·048

If one refers to the Fourier projection $\rho(y, z)$, one will find a resolved peak in the neighborhood of (0·052, 0·064), and an unresolved one which covers the atom $O_{1-\mathrm{II}}$ and the proximate carbon atom in the projected structure.

The Mn–O distance based on this tentative parameter assignment is 2·00 Å.

Structure factors were calculated with inclusion of the eight atoms. They are appended as entry B in Tables 2 and 3. The values of the expression

$$\Sigma\,|\,|F|_o - |F|_c \div \Sigma\,|F|_o$$

are 13·5 and 34 % respectively (absent reflections are neglected).

(4) *The description of the pseudo structure*

The structure based on the final values of the parameters is shown in Figs. 10 and 11. Each atom is labeled by a first Arabic numeral referring to the complex molecule, a second Arabic numeral specifying the atom, and a Roman numeral in the third position referring to one or the other enantiomorphic half of the complex molecule.

The approximate parameters of the 25 atoms in the complex molecule 1 are given in Table 4.

Table 4. *Approximate parameters*

	x	y	z
Mn_1	0·500	0·119	0·008
$Cl_{1-\mathrm{I}}$	0·684	0·128	−0·155
$O_{1-\mathrm{I}}$	0·610	0·052	0·064
$N_{1-1-\mathrm{I}}$	0·536	0·206	0·198
$N_{1-2-\mathrm{I}}$	0·507	0·313	0·227
$N_{1-3-\mathrm{I}}$	0·507	0·249	0·496
$N_{1-4-\mathrm{I}}$	0·683	0·268	0·334
$C_{1-1-\mathrm{I}}$	0·492	0·259	0·122
$C_{1-2-\mathrm{I}}$	0·492	0·199	0·379
$C_{1-3-\mathrm{I}}$	0·657	0·217	0·222
$C_{1-4-\mathrm{I}}$	0·630	0·318	0·249
$C_{1-5-\mathrm{I}}$	0·630	0·258	0·502
$C_{1-6-\mathrm{I}}$	0·465	0·303	0·409
$Cl_{1-\mathrm{II}}$	0·316	0·110	0·172
$O_{1-\mathrm{II}}$	0·390	0·186	0·048
$N_{1-1-\mathrm{II}}$	0·464	0·032	−0·183
$N_{1-2-\mathrm{II}}$	0·493	−0·076	−0·212
$N_{1-3-\mathrm{II}}$	0·493	−0·012	−0·480
$N_{1-4-\mathrm{II}}$	0·317	−0·030	−0·319
$C_{1-1-\mathrm{II}}$	0·508	−0·022	−0·106
$C_{1-2-\mathrm{II}}$	0·508	0·038	−0·363
$C_{1-3-\mathrm{II}}$	0·343	0·021	−0·205
$C_{1-4-\mathrm{II}}$	0·370	−0·080	−0·231
$C_{1-5-\mathrm{II}}$	0·370	−0·019	−0·487
$C_{1-6-\mathrm{II}}$	0·535	−0·065	−0·392

Fig. 12 shows a complex molecule. The bond angle between the Mn–Cl and Mn–N bonds is calculated to be 93° 50′. The deviation from 90° is within the limits of experimental error. There are six mirror planes in each HMT molecule. The orientation of the two HMT molecules in the complex molecule is almost such that one of the mirror planes of each HMT molecule is perpendicular to the plane of the Mn–N and Mn–Cl bonds. The manganese atom lies exactly on the common three-fold axis of the two HMT molecules at the center of symmetry of the complex molecule. Bond distances are also shown in Fig. 12.

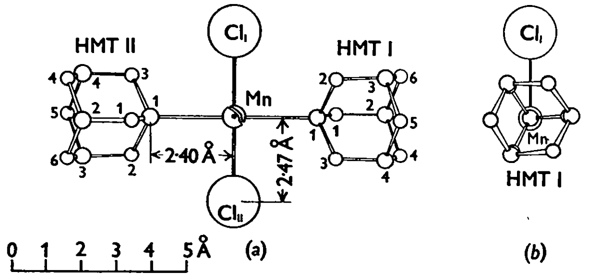

Fig. 12. (*a*) A complex molecule; (*b*) the right half of a complex molecule. The bonds from manganese to the two oxygen atoms (not shown) extend normal to the plane in (*a*); Mn–O = 2·00 Å.

7. Conclusions

In view of the evidence provided by the Patterson functions, structure factors, and Fourier syntheses the pseudo structure described in Figs. 10 and 11 and analytically in Table 4 is a highly probable one. While the evidence regarding the anhydrous part of the complex molecules is sufficiently conclusive, the determination of the positions of the oxygen atoms needs further evidence in addition to that presented in § 6 (3).

The structure found in this work for the HMT complex with manganous chloride explains its stability. The structure also proves the analogy between the HMT and ammonia complexes in that the HMT molecule interacts with the manganese atom through the unshared pair of electrons of one of its four nitrogen atoms. This type of bonding may have considerable generality in the HMT complexes.

Pauling's magnetic criterion predicts five unpaired electrons for the manganese atom forming ionic bonds and covalent bonds of the type $4s4p^3 4d^2$, and five were found experimentally. Appropriate bond distances were observed.

The relation between the pseudo structure based on the pseudo unit cell and the exact structure based on the true unit cell is not entirely clear, nor is the nature of the fairly strong streaks occurring on many Weissenberg photographs. Very likely the difference between the two structures lies only in the relative positions of the complex molecules rather than in the configuration within a given complex molecule.

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