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The Structure of Manganese Dichloride Tetrahydrate: A Neutron-Diffraction Study*

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The hydrogen atoms in the room-temperature form of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ have been located by neutron-diffraction analysis. The data provide independent confirmation and refinement of the hydrogen positions and hydrogen-bonding scheme deduced by Baur by consideration of the electrostatic energy of the crystal, utilizing the results of the X-ray analysis of Zalkin and co-workers. The H-O-H angles in the 4 different water molecules are 104.3, 106.1, 111.4, and 112.4° (standard deviation about 0.3° for each). One hydrogen bond is clearly bifurcated, as deduced by Baur; in addition, there is another atomic configuration which may be regarded as a very unevenly bifurcated hydrogen bond. Among the remaining hydrogen bonds there are significant departures from linearity (by as much as 21°). The heavy-atom coordinates are not significantly different from those from the work of Zalkin *et al.*; however, some of the thermal parameters are significantly different. In the least-squares refinement scattering factors (relative to the factor for H) for Mn, O, and Cl were obtained which are slightly different from those previously tabulated.

Introduction

Neutron-diffraction analysis of the room-temperature (α) form of manganese dichloride tetrahydrate ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$) was undertaken to locate the hydrogen atoms as accurately as possible. Reliable hydrogen coordinates were required both for establishing the pattern of hydrogen bonding and for possible use in connection with nuclear magnetic resonance (n.m.r.) studies of the substance in its antiferromagnetic state.

The heavy-atom structure of the α form of manganese chloride tetrahydrate was determined precisely in an X-ray analysis by Zalkin, Forrester & Templeton (1964), and a set of approximate coordinates for the hydrogen atoms was obtained in the final stages of the analysis. A previous attempt at neutron-diffraction

analysis of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ was reported briefly (Gardner, 1960), but final results have not been published. An n.m.r. study of the compound at room temperature (El Saffar, 1965) did not furnish proton-proton vectors; the spectrum is unusual, there being only a single bell-shaped peak with a width of about 12 gauss and no dipole-dipole splitting.

Because of an error in the use of a computer program, Zalkin *et al.* did not give a complete description of the hydrogen bonding. Baur (1965a) showed, however, that all of their eight experimental positions for the hydrogen atoms except the position for H(32) fit into a reasonable hydrogen bonding scheme. Baur also calculated the hydrogen positions of least electrostatic energy consistent with the known heavy-atom positions and with assumed values for the H-O-H angle and the O-H bond length, using a procedure with which he had previously been successful in predicting hydrogen positions in close agreement with those from neutron diffraction (Baur, 1965b). For atom H(32) a new position 0.73 Å from the X-ray position was

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found which fits into the hydrogen-bonding scheme; for the other hydrogen atoms the agreement was fair (average shift, 0.21 Å). Baur considers his proposed positions to be better approximations to the actual positions than those from the X-ray diffraction study. Our determination of the hydrogen-atom coordinates confirms his expectations.

Manganese dichloride tetrahydrate is antiferromagnetic at temperatures below 1.62°K (Friedberg & Wasscher, 1953; Henry, 1953). N.m.r. data are often used in conjunction with atomic positions to determine magnetic space groups. Accurately determined hydrogen positions are essential in correlating the calculated local fields for possible color groups with the observed local fields at the proton sites (*cf.* Spence, Middents, El Saffar & Kleinberg, 1964; Spence & Nagarajan, 1966). The hydrogen positions determined in the present neutron-diffraction study have already been useful to Spence & Nagarajan (1966) in an n.m.r. study of the magnetic structure of MnCl₂·4H₂O in its antiferromagnetic state.

Data

A crystal specimen weighing 57.9 mg was cut from a larger specimen grown from aqueous solution at room temperature. It was an almost regular hexagonal plate, 1.5 mm thick and 2 mm on a side. The large faces were of the form {100}. The axis *b* was approximately perpendicular to one of the 1.5 × 2 mm faces. The crystal was subjected to thermal shocks by repeatedly dipping it into liquid nitrogen, in the hope of reducing secondary extinction effects. Preliminary X-ray precession photography established that it was a single crystal. The specimen was mounted on a goniometer head with the *b* axis parallel to the spindle and then sealed inside a thin-walled tube of quartz for protection from moisture.

Intensity data were recorded with the Oak Ridge automatic single-crystal neutron diffractometer (Busing, Smith, Peterson & Levy, 1964) by the θ -2 θ step-scan method to 111.4° in 2 θ , the limit of the instrument. The neutron wavelength was 1.078 Å. A total of 2991 observations were made, corresponding to 2328 independent reflections. In every significant respect the procedures followed in recording the data and in the subsequent preliminary data processing were those used by Brown & Walker (1966) in a study of K₂NbF₇ and described in more detail earlier by Brown & Levy (1964). The variance σ^2 of each observation F_o^2 as derived from counting statistics was modified by the addition of an empirical correction term (0.03 F^2)², as is usual in this laboratory. The linear absorption coefficient of MnCl₂·4H₂O for the neutron wavelength used was determined experimentally to be 2.35 cm⁻¹. Correction factors for absorption, calculated with the program of Wehe, Busing & Levy (1962), were in the range 1.56 to 2.17.

Throughout this work we have used the unit-cell

parameters* and space group established by Zalkin *et al.* (1964): $a=11.186$ (6), $b=9.513$ (5), $c=6.186$ (2) Å, $\beta=99.74$ (4)°, space group $P2_1/n$, four units MnCl₂·4H₂O per cell.

Refinement of the structure

Refinement was carried out by the method of least squares, with a local version of the full-matrix least-squares program of Busing, Martin & Levy (1962). The function minimized was $\sum w(F_o^2 - S^2 F_c^2)^2$, where F_o^2 and F_c^2 are the observed and calculated structure-factor squares, S is the scale factor on the calculated values F_c , and the weight w is the reciprocal of the variance of F_o^2 . The refinement was started using the atomic parameters from the X-ray analysis. The neutron coherent scattering amplitudes originally used were those of Bacon (1962). Eventually, the following parameters were refined to convergence: the scale factor S ; 3 coordinates and 6 parameters† of anisotropic thermal motion for each atom; the scattering factors of Mn, Cl and O. The scattering factor of hydrogen was held fixed.

A number of the values F_o^2 for reflections of high intensity were obviously in error because of extinction. The full extent of the errors as a function of the observed intensity I_o (where $I_o = F_o^2 / \sin 2\theta$) was assessed by the procedure used by Brown & Walker (1966) in dealing with extinction in K₂NbF₇. In the final cycles of the refinement the 224 reflections of highest intensity ($I_o > 20 \times 10^{-24}$ cm²) were omitted. The maximum effect of extinction was to reduce $|F_o|$ relative to $|F_c|$ by about 17%. Another 77 reflections (all very weak) were omitted because their phase signs were considered indeterminate. In the final least-squares cycle no parameter shift exceeded 5×10^{-6} in magnitude. The final values of the discrepancy indices‡ $R(F)$ and $R(F^2)$ are the same, 0.076; R_w is 0.088; the standard deviation of an observation of unit weight,§ σ_1 , is 1.12. When, for the same structure parameters, the contributions of 344 additional weak reflections, for which $F_o^2 \leq \sigma(F_o^2)$, are excluded the values of $R(F)$, $R(F^2)$, R_w , and σ_1 become 0.055, 0.071, 0.086 and 1.20 respectively. When all data are included in the calculation of the discrepancy indices, $R(F)$, $R(F^2)$, R_w , and σ_1 become 0.072, 0.086, 0.095 and 1.44 respectively.

As a check on the correctness of the structure, a

* Here and elsewhere in this paper the standard error of a parameter appears in parentheses next to the value of the parameter. The digits in parentheses correspond to the least-significant digits of the parameter.

† These are the parameters β_{ij} in the temperature factor $\exp[-h^2\beta_{11} - k^2\beta_{22} - l^2\beta_{33} - 2hk\beta_{12} - 2hl\beta_{13} - 2kl\beta_{23}]$.

‡ $R(F)$ and $R(F^2)$ are defined by the equation $R(F^x) = \sum |F_o^x - S^x F_c^x| / \sum |F_o^x|$. The weighted index R_w is given by $R_w = [\sum w(F_o^2 - S^2 F_c^2)^2 / \sum w F_o^4]^{1/2}$.

§ The standard deviation of an observation of unit weight is defined by $\sigma_1 = [\sum w(F_o^2 - S^2 F_c^2)^2 / (n - p)]^{1/2}$, where n is the number of observations and p is the number of parameters fitted to the data.

Table 3. Neutron scattering amplitudes (in units of 10^{-12} cm) for manganese, chlorine and oxygen

Values have been rescaled to the value -0.372 for hydrogen as necessary.

	Bacon (1962)	This laboratory	Bacon (1969)
Mn	-0.354	-0.373 (3) ^a	-0.36
Cl	0.974	0.959 (6) ^a	0.96
		0.947 (5) ^b	
		0.951 (5) ^c	
		0.971 (5) ^d	
		Avg. 0.957 [9] ^e	
O	0.568	0.583 (4) ^a	0.577
		0.581 (3) ^b	
		0.576 (3) ^c	
		0.586 (2) ^d	
		0.579 (3) ^e	
		0.579 (3) ^f	
		0.592 (3) ^g	
		Avg. 0.582 (2) ^h	
		Avg. 0.582 [5] ⁱ	

^a $\text{MnCl}_4 \cdot 4\text{H}_2\text{O}$, this work.

^b Chloral hydrate (Brown & Levy, 1970).

^c Potassium hydrogen chloromaleate (Ellison & Levy, 1965). On the scale used in the original report f_0 was given inadvertently as 0.586 instead of 0.568×10^{-12} .

^d Magnesium chloride hexahydrate (Agron & Busing, 1969).

^e Copper ammonium sulfate hexahydrate (Brown & Chidambaram, 1969).

^f Cupric acetate monohydrate (Chidambaram & Brown, 1970).

^g Uronium nitrate (Worsham & Busing, 1969).

^h Glycolic acid (Ellison & Levy, 1970).

ⁱ Bracketed numbers specify root-mean-square deviations from averages.

Discussion

Scattering factors

Our final scattering factors (see Table 3) appear to be significantly different from those used initially. The R -factor ratio test (Hamilton, 1965) shows that the improvement in agreement between the F_o^2 and F_c^2 values accompanying the adjustment of scattering-factors is significant at the 0.995 probability level ($R=1.034$, $R_3, 1888$, $0.005=1.003$). The final scattering

Table 4. Description of atomic thermal-parameter ellipsoids of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, orientations of the principal axes and root-mean-square axial displacements

The orientations of the principal axes are specified with respect to the unit vectors i, j, k of a Cartesian coordinate system and to interatomic vectors $X \rightarrow A$. The vector i is along the crystal vector a ; j is along c^* ; k is along b . Atom X is the atom to which atom A is coordinated or bonded.

ATOM	P.A.	R.M.S.D. (Å)	ANGLE (°) BETWEEN P.A. AND REFERENCE AXIS				R.M.S.D. OF X AND A ALONG X → A	
			i	j	k	X → A	X	A
Mn	1	0.131 (2)	46 (15)	130 (19)	108 (8)			
	2	0.135 (2)	124 (17)	139 (19)	71 (9)			
	3	0.145 (2)	117 (6)	93 (7)	153 (7)			
Cl(1)	1	0.134 (1)	30 (1)	104 (1)	64 (1)	91 (1)	0.135 (2) 0.183 (1)	
	2	0.173 (1)	116 (1)	142 (1)	65 (1)	43 (2)		
	3	0.194 (1)	76 (1)	24 (1)	142 (1)	47 (2)		
Cl(2)	1	0.138 (1)	40 (1)	86 (1)	130 (1)	65 (1)	0.132 (2) 0.169 (1)	
	2	0.164 (1)	54 (1)	71 (2)	42 (1)	105 (2)		
	3	0.176 (1)	105 (2)	19 (2)	102 (2)	151 (1)		
O(1)	1	0.139 (1)	82 (1)	28 (2)	63 (2)	136 (1)	0.133 (2) 0.161 (1)	
	2	0.170 (1)	116 (4)	111 (2)	34 (3)	73 (3)		
	3	0.185 (1)	27 (4)	108 (2)	71 (3)	51 (2)		
O(2)	1	0.140 (1)	84 (3)	6 (3)	88 (1)	166 (1)	0.136 (2) 0.144 (1)	
	2	0.158 (1)	161 (2)	85 (3)	72 (2)	87 (3)		
	3	0.193 (1)	108 (1)	87 (1)	162 (2)	76 (1)		
O(3)	1	0.143 (1)	54 (1)	89 (1)	144 (1)	44 (1)	0.144 (2) 0.190 (1)	
	2	0.184 (1)	68 (1)	153 (1)	75 (1)	107 (1)		
	3	0.237 (1)	45 (1)	63 (1)	58 (1)	130 (1)		
O(4)	1	0.148 (1)	38 (2)	115 (1)	64 (2)	10 (2)	0.141 (2) 0.149 (1)	
	2	0.178 (1)	116 (2)	84 (1)	27 (2)	81 (2)		
	3	0.222 (1)	65 (1)	26 (1)	85 (1)	85 (1)		
H(11)	1	0.187 (3)	31 (3)	59 (3)	90 (1)	19 (2)	0.173 (1) 0.196 (3)	
	2	0.219 (3)	59 (3)	149 (3)	87 (2)	82 (3)		
	3	0.268 (3)	81 (2)	93 (2)	177 (2)	73 (1)		
H(12)	1	0.169 (3)	90 (1)	122 (2)	148 (2)	160 (2)	0.160 (1) 0.177 (3)	
	2	0.228 (3)	104 (1)	145 (2)	59 (2)	70 (2)		
	3	0.392 (4)	14 (1)	102 (1)	83 (1)	88 (1)		
H(21)	1	0.169 (2)	32 (2)	61 (2)	103 (2)	167 (2)	0.156 (1) 0.172 (2)	
	2	0.217 (2)	71 (3)	143 (3)	120 (4)	103 (2)		
	3	0.241 (3)	115 (2)	70 (4)	147 (4)	87 (2)		
H(22)	1	0.165 (3)	116 (2)	26 (1)	94 (1)	160 (1)	0.162 (1) 0.180 (2)	
	2	0.228 (2)	149 (2)	113 (2)	70 (2)	98 (2)		
	3	0.277 (3)	106 (2)	102 (1)	160 (2)	108 (1)		
H(31)	1	0.173 (3)	73 (1)	53 (1)	138 (1)	154 (1)	0.180 (2) 0.199 (3)	
	2	0.257 (3)	150 (4)	100 (4)	118 (3)	89 (2)		
	3	0.285 (3)	114 (4)	39 (2)	62 (3)	116 (1)		
H(32)	1	0.178 (3)	50 (1)	118 (1)	127 (2)	61 (1)	0.191 (1) 0.298 (4)	
	2	0.258 (3)	69 (2)	121 (1)	39 (2)	52 (1)		
	3	0.381 (4)	47 (1)	44 (1)	80 (1)	129 (1)		
H(41)	1	0.173 (3)	19 (1)	109 (1)	90 (1)	21 (1)	0.164 (1) 0.187 (3)	
	2	0.259 (3)	98 (3)	115 (9)	27 (10)	105 (3)		
	3	0.272 (3)	73 (2)	32 (8)	63 (10)	104 (3)		
H(42)	1	0.180 (3)	108 (2)	74 (1)	156 (2)	24 (2)	0.173 (2) 0.195 (3)	
	2	0.235 (3)	159 (3)	106 (4)	76 (2)	103 (2)		
	3	0.266 (3)	101 (4)	23 (3)	70 (2)	110 (2)		

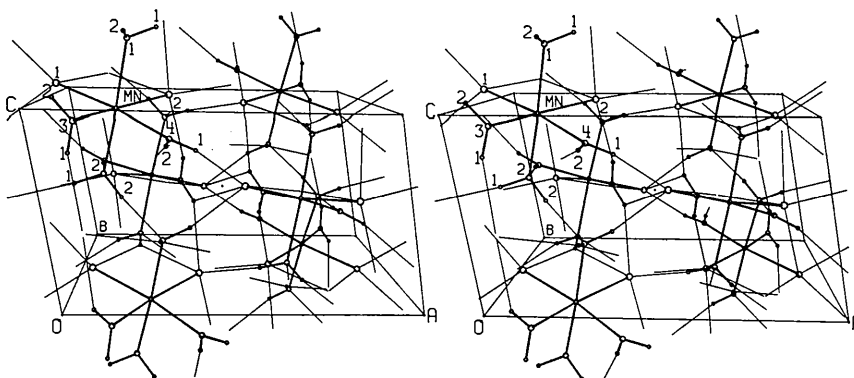


Fig. 1. Stereoscopic drawing of the crystal structure of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$. The direction of view makes angles of 0° with a , 11° with b , and 101° with c^* . The manganese atom is labelled MN; the chlorine and oxygen atoms are labelled with the appropriate numbers that appear in parentheses in Table 2; hydrogen (1) on oxygen (2) means H(21) in Table 2, and so forth.

Table 5. Distances and angles in the octahedron around the manganese ion of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$

Standard errors are about 0.0015 Å and 0.05°.

	Distance or angle
Mn-Cl(1)	2.500 Å
Mn-Cl(2)	2.476
Mn-O(1)	2.223
Mn-O(2)	2.218
Mn-O(3)	2.187
Mn-O(4)	2.202
Cl(1)-Mn-Cl(2)	96.3°
Cl(1)-Mn-O(1)	91.5
Cl(1)-Mn-O(2)	86.5
Cl(1)-Mn-O(3)	93.4
Cl(1)-Mn-O(4)	173.7
Cl(2)-Mn-O(1)	87.5
Cl(2)-Mn-O(2)	94.3
Cl(2)-Mn-O(3)	169.0
Cl(2)-Mn-O(4)	89.0
O(1)-Mn-O(2)	177.4
O(1)-Mn-O(3)	86.9
O(1)-Mn-O(4)	92.0
O(2)-Mn-O(3)	91.5
O(2)-Mn-O(4)	89.7
O(3)-Mn-O(4)	81.7

factors also seem to be in better overall agreement with those of Bacon (1969) than with those of Bacon (1962).

It may be appropriate, following the emphasis just given to small differences in scattering factors, to view the matter in a different perspective by summarizing the shifts in derived structural parameters which occurred when the scattering factors were adjusted. For the heavy atoms, the maximum and mean coordinate shifts are 0.0008 and 0.0003 Å (0.8 and 0.3 times the corresponding coordinate standard errors). The heavy-atom β_{ii} parameters changed somewhat more: Mn, $\sim +4\sigma$; Cl, -2σ to -3σ ; O, $+2\sigma$ to $+3\sigma$. The β_{ij} parameter changes were much smaller. Among the hydrogen atoms the maximum and mean coordinate changes were 0.0044 and 0.0012 Å (1σ and 0.4σ). The hydrogen thermal parameter changes were small: maximum, 1σ ; average, 0.4σ .

The heavy-atom structure

Although the discrepancy index $R(F)$ of the neutron refinement is about twice that of the X-ray determination of Zalkin *et al.*, the neutron parameters overall appear to be considerably more precise than the X-ray parameters. The standard errors of the manganese and chlorine coordinates and the manganese thermal parameters are about the same, but for the other parameters the errors from the X-ray analysis are from 3 to 8 times those from the neutron analysis. The lower precision in the X-ray work probably results in part from the smaller number of observations and in part from the inadequacies of available X-ray scattering-factor functions, but mainly from the inherent decline in magnitude of the X-ray scattering factors with angle, which renders the high-angle data relatively less sensitive to the parameters. The lower $R(F)$ value associated

with the determination of lower precision merely emphasizes the known deficiency of $R(F)$ as a measure of the precision of a determination.

The average and maximum values of $|A|$ for the coordinates (see Table 2) are 0.0021 and 0.0039 Å; the average and maximum $|A|/\sigma$ values are 0.8 and 1.9. The R -factor ratio test shows that our coordinates do not fit our data significantly better than the coordinates from the X-ray analysis (probability level ~ 0.5). The two sets of coordinates must, therefore, be considered to be in excellent agreement.

The agreement is much less satisfactory for the thermal parameters, especially for the β_{11} terms. For these the minimum, mean, and maximum values of $|A|/\sigma$ are 2.3, 5.3 and 8.8, all of the β_{11} values being higher in the X-ray parameter set than in the neutron set (as is also the case for all of the β_{22} parameters and all except one of the β_{33} parameters). The R -factor ratio test shows that our thermal parameters fit our data much better than those from the X-ray analysis ($R=2.55$, $R_{2, 1888, 0.005}=1.17$, probability ≥ 0.995). When the test is made separately for the thermal parameters of each kind of heavy atom, we again find that our parameters fit our data significantly better in each case (probability level 0.995, or higher). For the manganese and oxygen atoms the agreement between X-ray and neutron thermal parameters is somewhat poorer if the neutron parameters reached before adjustment of scattering factors are used; for the chlorine atoms it is slightly better.

The discrepancies in thermal parameters imply slight systematic errors in either the X-ray determination or in the neutron determination, or in both. However, it is not clear to us what sort of error can have the effect of producing discrepancies mainly in the β_{11} parameters. In principle, of course, with a crystal of inappropriate size, shape, and orientation, such an effect could result from neglect of absorption errors or from improper computation of absorption corrections. Absorption was neglected in the X-ray work, but the small size of the crystal (maximum dimension 0.1 mm) and the moderate absorption coefficient ($\mu=28 \text{ cm}^{-1}$) suggest that negligible error should result from this source. The absorption corrections used in the neutron work should be reliable. The simple geometric shape made it easy to measure the crystal accurately, and an experimental value of the absorption coefficient was used.

The bond distances and angles (see Table 5) within the octahedron of oxygen and chlorine atoms around the manganese ion, are, of course, almost identical with those reported by Zalkin *et al.* For the bond lengths the largest discrepancy is that of bond Mn-O(2), 0.009 Å.

Hydrogen atoms, water molecules, and hydrogen bonding

On the average our hydrogen positions differ from those of Zalkin *et al.* by 0.26 Å, which is about what one might expect in view of the standard errors estimated in the X-ray analysis. They differ on the average

by only 0.09 Å from the positions of least electrostatic energy of Baur (1965a). Our results, therefore, seem to confirm the validity of Baur's procedure for calculating hydrogen positions. They also re-emphasize the well-known superiority of the neutron method over the X-ray method in locating hydrogen atoms.

The O-H bond lengths (see Table 6) show a considerable range of values, from 0.923 to 0.971 Å, reflecting widely varying perturbation effects of thermal motion, or, from another point of view, reflecting varying strengths of hydrogen bonding for the different hydrogen atoms. The O-H bond lengths and the oxygen valence angles, which vary from 104.3 to 112.4°, show about the same ranges of values as have been found in three-dimensional neutron-diffraction analyses of other inorganic hydrates in this laboratory (BaCl₂·2H₂O, Padmanabhan, Busing & Levy, 1963; Cu₂(CH₃COO)₄·2H₂O, Chidambaram & Brown, 1970; Cu(NH₄)₂(SO₄)₂·6H₂O, Brown & Chidambaram, 1969). We have 'corrected' the O-H bond lengths (see values in parentheses in Table 6) on the assumption that the hydrogen atoms 'ride' (Busing & Levy, 1964) the oxygen atoms. The assumption can only be valid as an approximation; consequently we do not consider the O-H bond lengths to be highly accurate.

The geometry of each of the hydrogen bonds is shown in Table 6. Four of the eight hydrogen atoms form normal (*i.e.* not bifurcated) hydrogen bonds to chlorine ions and two form normal hydrogen bonds to oxygen atoms. Among these hydrogen bonds there are considerable departures from linearity. Atom H(12) forms a bifurcated bond from O(1) to Cl(1) and Cl(2), just as proposed by Baur. The four atoms involved lie in a plane: the sum of the angles O(1)-H(12)-Cl(1), O(1)-H(12)-Cl(2), and Cl(1)-H(12)-Cl(2) is 360.0°. The configuration defined by atoms O(3), H(32), Cl(1) and Cl(2) should, we think, be regarded as an extremely unevenly bifurcated hydrogen bond - or perhaps as a case of incipient bifurcation, since the interaction between H(32) and Cl(1) separated by 2.95 Å must be quite weak. The four atoms in this configuration are not quite coplanar: the sum of the angles about atom H(32) is 356.9°.

Our finding in this crystal structure of hydrogen bonds bent to various degrees and of one rather evenly bifurcated bond and one unevenly bifurcated bond supports Baur's (1965b) thesis 'that there are no sharp limits between the geometrically different types of hydrogen bond'.

On the whole, the hydrogen-bonding interactions just described are somewhat weak, judged by the distances H...Cl and H...O. The bifurcated bonds are especially weak, as is indicated also by the large vibrational amplitudes of the hydrogen atoms H(12) and H(32) and by the shortening of the apparent bond lengths O(1)-H(12) and O(3)-H(32) resulting from the perturbing effects of the thermal motion. Thermal motion is probably responsible for the fact that dipole-dipole splittings of the n.m.r. lines are not observed

Table 6. Detailed geometry of the water molecules and of the hydrogen bonds in the crystal structure of MnCl₂·4H₂O

Interatomic distances are in Å; angles are in degrees. The standard errors of the distances are: O-H, 0.002 to 0.003; H...H, 0.003 to 0.004; O...O and O...Cl, 0.001 to 0.002; H...O and H...Cl, 0.002 to 0.004 Å. The standard errors of the angles are 0.2 to 0.4°.

HYDROGEN BOND	H ₂ O PARAMETERS			HYDROGEN-BOND PARAMETERS			
	DISTANCES		ANGLE	DISTANCES		ANGLES	
O-H-----X	O-H	H-H	H-O-H	O-X	H...X	O-H...X	X---O...X
O(1) 	0.967 (1.000)	1.509	104.3	3.173	2.227	165.7	126.8
	0.944 (1.021)			3.281	2.499	140.3	
O(2) 	0.971 (0.995)	1.546	106.1	3.168	2.201	174.1	112.3
	0.963 (0.999)			2.923	1.967	170.4	
O(3) 	0.955 (0.986)	1.561	112.4	3.202	2.294	158.7	74.5
	0.923 (0.989)			3.317	2.495	148.3	
O(4) 	0.941 (0.973)	1.565	111.4	3.291	2.374	164.4	120.2
	0.953 (0.978)			2.964	2.014	174.4	

at room temperature, in contrast, for example, to the case of BaCl₂·2H₂O (El Saffar, 1966), in which the hydrogen bonding is generally somewhat stronger.

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The Crystal and Molecular Structure of Bis(dimethyl-*o*-thiophenylarsine)platinum(II)

BY J. P. BEALE AND N. C. STEPHENSON

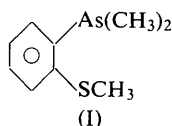
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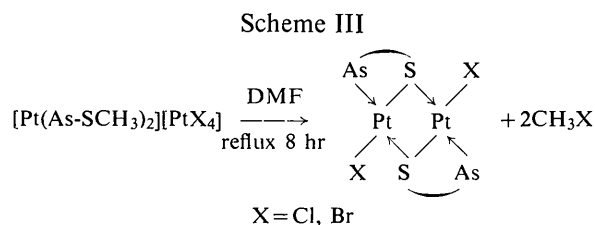
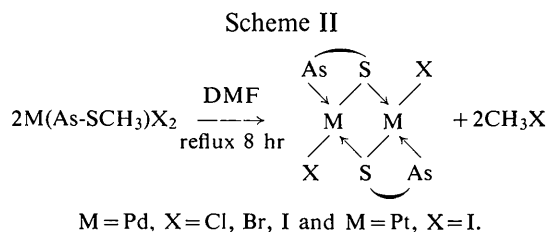
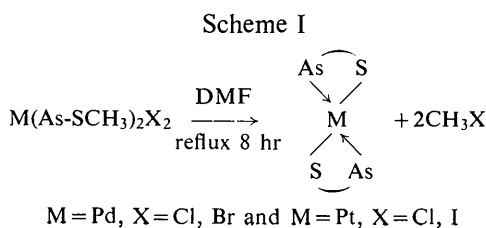
The crystal structure of the platinum thiol resulting from *S*-demethylation of the ligand dimethyl-*o*-methylthiophenylarsine has been examined using three-dimensional X-ray data collected initially by photographic techniques and finally on a Siemens automatic single-crystal diffractometer. The complex crystallizes in the monoclinic space group $P2_1/c$ with two molecules in a unit cell of dimensions $a = 7.818$ (2), $b = 9.662$ (2), $c = 13.052$ (3) Å, $\beta = 102.84$ (6)°. The molecule is a *trans* isomer in which the thiol functions as a bidentate ligand. The molecule is planar and the Pt-As bond distance is short, indicating $d\pi-d\pi$ bonding between the platinum atom and the thio-arsenic chelate.

Introduction

Mono and bis chelated complexes of dimethyl-*o*-methylthiophenylarsine (I) (As-SCH₃) of the types



$\text{Pd}(\text{As-SCH}_3)_2\text{X}_2$, $\text{M}(\text{As-SCH}_3)_2\text{X}_2$ (M = Pd, Pt; X = Cl, Br, I), $\text{Pt}(\text{As-SCH}_3)_2$ and $[\text{Pt}(\text{As-SCH}_3)_2][\text{PtX}_4]$ (X = Cl, Br) have been reported (Livingstone, 1958; Chiswell & Livingstone, 1960). *S*-Demethylation of the ligand occurs when these compounds are heated under reflux in dimethylformamide (DMF), as shown in schemes I-III (Lindoy, Livingstone & Lockyer, 1967).



There are interesting structural implications involved with these schemes. Thus, in scheme I, the compounds $\text{M}(\text{As-SCH}_3)_2\text{X}_2$ might well be examples of six-coordinate, diamagnetic d^8 complexes. Verification of octahedral coordination in these compounds has been limited (Stephenson, 1962; Stephenson & Jeffrey, 1963; Duckworth & Stephenson, 1969). In fact $\text{Pd}(\text{As-SCH}_3)_2\text{I}_2$