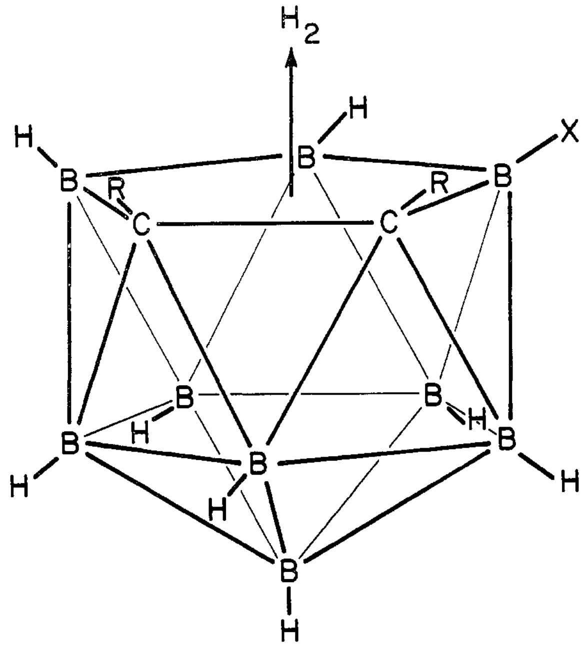

Figure 2.—A proposed structure for $B_9C_2H_{12}I$ where X = iodine.

nine boron atoms nonequivalent and lead to a spectrum which contained more than one doublet of relative intensity 1 (ideally, eight doublets would appear at high resolution). These arguments assume that the two extra protons present in $B_9C_2H_{12}I$ are only weakly coupled with their neighboring boron atoms in the open face. Since at least three doublets of relative intensity 1 are seen in the ^{11}B n.m.r. spectrum of $B_9C_2H_{12}I$, the latter structure is preferred. In addition, the ^1H n.m.r. signal which represents CH_3 protons in the C,C′-dimethyl derivative is rather broad and suggests that the two methyl groups are nonequivalent in the anion and this gives additional support to the proposed structure.

The iodination of $B_9C_2H_{12}^-$ is probably best viewed as an electrophilic substitution by I_2. In agreement with this concept, aryldiazonium ions (weak electrophiles) give intensely colored products in the presence of $B_9C_2H_{12}^-$ which are strongly reminiscent of the products of aryldiazonium ions on $B_{10}H_{10}^{-2}$.[6,7]

The bromine in $B_9C_2H_{11}Br^-$ was not particularly prone to nucleophilic displacement as shown by the recovery of unreacted $B_9C_2H_{11}Br^-(CH_3)_4N^+$ after 50 hr. reflux in acetone saturated with KI. Pyrolysis of the cesium salt of $B_9C_2H_{11}I^-$ produced CsI (85%) and the previously reported[3] $B_9C_2H_{11}$ (25%).

$B_9C_2H_{12}I$ is extremely hygroscopic and can only be handled in a water-free atmosphere. It decomposes at 70–71° with the evolution of H_2. The product obtained upon decomposition of the dry solid appears to be polymeric rather than the $B_9C_2H_{10}I$ which might be anticipated.

Acknowledgments.—The authors wish to thank the Alfred P. Sloan Foundation and the Army Research Office (Durham) for generous support of this work.

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(6) M. F. Hawthorne and F. P. Olsen, *J. Am. Chem. Soc.*, **86**, 4219 (1964).

(7) M. F. Hawthorne and F. P. Olsen, *ibid.*, **87**, 2366 (1965).

Correspondence

Hydrogen Bonding in Manganese Dichloride Tetrahydrate

Sir:

In a recent paper on the crystal structure determination of $MnCl_2 \cdot 4H_2O$[1] a hydrogen-bonding scheme for this compound, based on a very accurate X-ray diffraction study, has been proposed. According to this study only four of the eight crystallographically different hydrogen atoms are involved in hydrogen bonds.[2] Although it is known that hydrogen atoms of water molecules do not always participate in hydrogen bonds (*e.g.*, the neutron diffraction study of $MgSO_4 \cdot 4H_2O$[3]), a closer inspection of the $MnCl_2 \cdot 4H_2O$ structure reveals that this is not the case here. Besides the four hydrogen bonds mentioned by Zalkin, Forrester, and Templeton (O(1)–H(11)···Cl(1), 3.17 Å.; O(2)–H(21)···Cl(2), 3.17 Å., O(2)–H(22)···O(1), 2.93 Å.; and O(4)–H(41)···Cl(1), 3.29 Å., where the distances are those between the water oxygen atoms and the acceptor atoms of the hydrogen bonds) four other hydrogen bonds can be shown to be possible. The oxygen atom O(1) has two more close neighbors, Cl(1) at 3.28 Å. and Cl(2) at 3.30 Å.; H(12) can form a bifurcated hydrogen bond to these chlorine atoms with a geometry similar to the one found for one of the hydrogen atoms in $BaCl_2 \cdot 2H_2O$ (according to a neutron diffraction investigation[4]). Atom O(3) has three close neighbors outside of the coordination polyhedron of the Mn^{2+} ion: Cl(2) at 3.20 and 3.32 Å. and O(3) at 3.13 Å. The latter distance cannot correspond to a hydrogen bond because the two O(3) atoms are related by a center of symmetry. The Cl(2)–O(3)–Cl(2) angle is 143°, which means that the O(3)–H···Cl(2) angles must be bent to 150°; a geometry similar to the one

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(1) A. Zalkin, J. D. Forrester, and D. H. Templeton, *Inorg. Chem.*, **3**, 529 (1964).

(2) In a private communication of April 13, 1965, Zalkin, Forrester, and Templeton state: "In our calculation of interatomic distances in $MnCl_2 \cdot 4H_2O$ we made an error in a data card which specified the symmetry. This error caused half of the atoms to be ignored in the search for neighbors, and we failed to find several of the hydrogen bonds which are correctly described by Baur."

(3) W. H. Baur, *Acta Cryst.*, **17**, 863 (1964).

(4) V. M. Padmanabhan, W. R. Busing, and H. A. Levy, *ibid.*, **16**, A26 (1963).

TABLE I

$MnCl_2 \cdot 4H_2O$, COMPARISON OF POSITIONAL PARAMETERS OF THE HYDROGEN ATOMS AS DETERMINED (I) EXPERIMENTALLY BY X-RAY DIFFRACTION[1] AND (II) BY CALCULATION OF POSITIONS OF LEAST ELECTROSTATIC ENERGY[a]

	I			II			d,
Atom	x	y	z	x	y	z	Å.
H(11)	0.39	0.15	0.37	0.382	0.141	0.402	0.25
H(12)	0.30	0.02	0.35	0.285	0.018	0.381	0.27
H(21)	0.08	0.20	0.62	0.072	0.202	0.606	0.11
H(22)	0.19	0.21	0.56	0.198	0.210	0.521	0.27
H(31)	0.11	0.95	0.87	0.102	0.927	0.821	0.37
H(32)	0.10	0.99	0.01	0.100	0.927	0.076	0.73
H(41)	0.43	0.09	0.81	0.436	0.072	0.801	0.20
H(42)	0.35	0.95	0.86	0.366	0.936	0.857	0.22

[a] d is the distance from the experimental to the calculated position (cell data[1]: a = 11.186 Å., b = 9.513 Å., c = 6.186 Å., β = 99.74°, Z = 4, space group $P2_1/n$).

around the water molecule in $Li_2SO_4 \cdot H_2O$ (according to a neutron diffraction study[5]). Atom O(4) has O(2) as another close neighbor at 2.96 Å. The angle Cl(1)–O(4)–O(2) is 120°. Thus it is not very different from the valence angle of the water molecule and the hydrogen bonds from O(4) to Cl(1) and O(2) can be approximately linear. These conclusions were reached solely by a consideration of the geometry of the O and Cl atomic positions. Except for H(32) all the experimental positions of the hydrogen atoms fit into this hydrogen-bonding scheme.

In order to test the assumptions made here about the distribution of the hydrogen bonds a second approach was tried. It has been shown[6] that the positions of hydrogen atoms of water molecules in crystalline hydrates can be predicted by calculating their positions of least electrostatic energy. In the case of $MgSO_4 \cdot 4H_2O$ the average distance between these calculated positions and positions determined experimentally by neutron diffraction is only 0.11 Å., which is better than the agreement found between the positions determined by X-ray[6,7] and neutron[3,6] diffraction (average distance 0.24 Å.). The positions of minimum electrostatic energy of the hydrogen atoms in $MnCl_2 \cdot 4H_2O$ were calculated, taking Mn^{2+} and Cl^- to be fully ionized and assuming an effective charge of -1.0 e on the oxygen atoms and of $+0.5$ e on each of the hydrogen atoms.[8] The shape of the water molecule was held fixed with an H–O–H angle of 109.5° and O–H distances of 0.97 Å. The calculated parameters of the hydrogen atoms are listed in Table I together with the experimental positions determined by Zalkin, *et al.* The agreement is generally fair, except for atom H(32). The position calculated for this atom appears to be more reasonable than the one found in the X-ray study. In the latter case H(32) is pointing toward the center of symmetry and thus toward the H(32) atom bonded to the centrosymmetrically related O(3) atom. An arrangement of this kind has hitherto not been described and it is very unlikely that hydrogen atoms should be next neighbors in this way, especially in this case where Cl(2) is within hydrogen-bonding distance from O(3). It is expected that the calculated positions of the hydrogen atoms in $MnCl_2 \cdot 4H_2O$ approximate their actual positions better than do the positions found by X-ray diffraction (as was found to be the case for $MgSO_4 \cdot 4H_2O$). This prediction will be verified or rejected when Gardner[9] publishes the full results of his neutron diffraction study of $MnCl_2 \cdot 4H_2O$.

TABLE II

GEOMETRY OF THE HYDROGEN BONDS IN $MnCl_2 \cdot 4H_2O$[a]

<table>
<tr><th></th><th></th><th colspan="2">Distances, Å.</th><th colspan="3">Angles, deg.</th></tr>
<tr><th></th><th>Y</th><th>O–Y</th><th>H...Y</th><th>O–H...Y</th><th colspan="2">Y(a)–O–Y(b)</th></tr>
<tr><td rowspan="3">O(1)</td><td>H(11)···Cl(1)</td><td>3.17</td><td>2.20</td><td>173</td><td rowspan="2">77</td><td rowspan="3">127</td></tr>
<tr><td>H(12)···Cl(1)</td><td>3.28</td><td>2.63</td><td>125</td></tr>
<tr><td>H(12)···Cl(2)</td><td>3.30</td><td>2.49</td><td>142</td><td></td></tr>
<tr><td rowspan="2">O(2)</td><td>H(21)···Cl(2)</td><td>3.17</td><td>2.20</td><td>177</td><td rowspan="2">112</td><td></td></tr>
<tr><td>H(22)···O(1)</td><td>2.93</td><td>2.00</td><td>160</td><td></td></tr>
<tr><td rowspan="2">O(3)</td><td>H(31)···Cl(2)</td><td>3.20</td><td>2.31</td><td>152</td><td rowspan="2">143</td><td></td></tr>
<tr><td>H(32)···Cl(2)</td><td>3.32</td><td>2.45</td><td>150</td><td></td></tr>
<tr><td rowspan="2">O(4)</td><td>H(41)···Cl(1)</td><td>3.29</td><td>2.34</td><td>166</td><td rowspan="2">120</td><td></td></tr>
<tr><td>H(42)···O(2)</td><td>2.96</td><td>2.00</td><td>174</td><td></td></tr>
</table>

[a] Y stands for the acceptor atom of the hydrogen bond. The calculated positions of the hydrogen atoms were used for computing the distances and angles.

Table II shows the geometry of the hydrogen bonds in $MnCl_2 \cdot 4H_2O$ as they are postulated here.[10]

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[5] H. G. Smith, S. W. Peterson, and H. A. Levy, Oak Ridge National Laboratory, Annual Progress Report, Chemistry Division, ORNL-3176, Oak Ridge, Tenn., 1961, p. 80.

[6] W. H. Baur, *Acta Cryst.*, in press.

[7] W. H. Baur, *ibid.*, **15**, 815 (1962).

[8] J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

[9] W. E. Gardner, *Bull. Am. Phys. Soc.*, **5**, 461 (1960).

[10] This work was supported in part by N. S. F. grant G-11309.

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Lability of Oxygen Atoms in Metal Carbonyls

Sir:

The oxygen atoms in metal carbonyls are thermodynamically strongly bonded and are rarely considered as kinetically labile nuclei. However, under certain conditions we find that the oxygen atoms in metal carbonyls undergo moderately fast exchange with the oxygen atoms in water. Rhenium hexacarbonyl cation, $Re(CO)_6^+$, dissolved in water containing 10.6 atom % O^{18} is significantly enriched in O^{18} within a matter of minutes. Exchange of all oxygen atoms in the carbonyl cation with those in the water is about 41% complete within 0.5 hr. In contrast, there is no detectable evidence of oxygen atom exchange between molybdenum hexacarbonyl and water within a 75-hr. period.

Oxygen atom exchange in $Re(CO)_6^+$ might proceed through a carboxylic acid intermediate of the type $(OC)_5ReCOOH$ or $[(OC)_5ReC(OH)_2]^+$ by attack of a carbon atom by OH^- or OH_2. There is precedent for