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			
Atom	x	y	z	x	y	z	d, 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., $\beta = 99.74°$, $Z = 4$, space group $P2_1/n$).

TABLE II

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

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

[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.

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 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).

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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 this in the reversible hydration of carbonyl derivatives of polyhedral boranes,[1] *e.g.*

$$B_{10}H_8(CO)_2 \overset{H_2O}{\rightleftarrows} B_{10}H_8CO(COOH)^- \overset{H_2O}{\rightleftarrows} B_{10}H_8(COOH)_2^{2-}$$

and in $Re(CO)_3(PR_3)_2COOR$ prepared from $Re(CO)_4(PR_3)_2$ and methoxide ion.[2] Attempts to characterize such an intermediate in the carbonyl system were unsuccessful, although addition of alkali to aqueous solutions of $Re(CO)_6^+AlCl_4^-$ yielded precipitates that displayed a normal metal carbonyl infrared stretching frequency at 1990 cm.$^{-1}$ as well as relatively sharp absorption at 1610 cm.$^{-1}$ that might be assigned to the carboxylic carbonyl stretching frequency.

The sharp difference in behavior between $Re(CO)_6^+$ and $Mo(CO)_6$ is a rather striking illustration of activation of a ligand site in a metal complex by formal positive charge. Earlier we reported similar activation of ligand sites in the alkaline hydrolysis of metal chelates derived from tropolone and from β-diketones.[3,4] There is the possibility of analogous activation in other metal complexes in which there are unsaturated sites within the ligand and electron delocalization in the metal–ligand system. By direct analogy to the metal carbonyl system one might expect an exchange, although at a low rate, of nitrogen atoms in cationic metal cyanides with the nitrogen atoms in ammonia solutions; the intermediate or activated complex could have an amidine-type function. Similarly, the oxygen atoms in metal nitrosyls may show lability with respect to water oxygen atoms in aqueous systems. Conversely, activation of ligand sites toward electrophiles may be achieved in certain anionic complexes. Thus, there is the possibility of a facile deuteration in anionic metal derivatives of cyclopentadiene in acidic aqueous media.

Triply-sublimed molybdenum hexacarbonyl (0.5 g.) was dissolved in 3 ml. of water containing 11.5 atom % O^{18} and 50 ml. of tetrahydrofuran. The solution was stirred for 75 hr. at 25°. Excess water was added to the solution to precipitate the hexacarbonyl which was recovered by filtration and then twice sublimed under vacuum. The carbonyl was oxidized in a Parr bomb calorimeter. Carbon dioxide was separated from excess oxygen by condensation and then analyzed for O^{18} content by mass spectrometry. There was no detectable increase in the *m/e* 46 peak over natural abundance.

The tetrachloroaluminate salt of rhenium hexacarbonyl[5] (1.76 g.) was dissolved in 10 g. of water containing 10.60 atom % O^{18}. The strongly acidic solution was stirred for 24 min. at 25° and quickly filtered. To the filtrate was added ferric chloride in a saturated hydrochloric acid solution, prepared from hydrogen chloride and water containing 10.60 atom % O^{18}, until a significant precipitate of $Re(CO)_6^+FeCl_4^-$ was present. The solid was collected on a sintered glass disk and partially dried by pressuring nitrogen through the sintered-disk funnel. Then, the solid was vacuum dried for 4 days at room temperature and finally at 40° (0.01 μ) for 3 hr. The weight of the solid was 1.2 g.[6] After this period of vacuum drying, an infrared spectrum of a heavy Nujol mull of the tetrachloroferrate salt showed only a possible trace of water of hydration. *Anal.* Calcd. for $Re(CO)_6^+FeCl_4^-$: Fe, 10.1; Cl, 25.7. Found: Fe, 10.3; Cl, 26.1. The carbonyl cation salt was oxidized as above, and mass spectroscopic analysis of the carbon dioxide indicated a $CO^{16}O^{18}$ content of 4.7 ± 0.2 mole %. Similar but cruder experiments were performed with reaction periods of about 1 hr.; O^{18} exchange was about 70% complete.

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[1] W. H. Knoth, J. C. Sauer, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **86**, 115 (1964).

[2] T. Kruck and M. Noack, *Chem. Ber.*, **97**, 1693 (1964). We are indebted to a referee for calling this reference to our attention.

[3] E. L. Muetterties and C. M. Wright, *J. Am. Chem. Soc.*, **86**, 5132 (1964).

[4] E. L. Muetterties and C. M. Wright, *ibid.*, **87**, 21 (1965).

[5] W. Hieber and T. Kruck, *Z. Naturforsch.*, **16b**, 709 (1961).

[6] Higher yields of the salts were obtained by adding excess tetrachloroferrate ion, but the precipitates obtained under these conditions were contaminated with the hydronium salt of $FeCl_4^-$, and water removal by vacuum drying proved extremely difficult.