nounced than was the case with $Co^{+2}$ and the relaxation times at three temperatures are given in Table I. The values of $\Delta H^*$ and $\Delta S^*$ were calculated to be $3.8^{+1.0}_{-0.6}$ kcal./mole and $-42^{+4}_{-2}$ e.u. The observed relaxation time was found to be independent of the concentrations of $Zn^{+2}$, $NO_3^-$, and $H^+$. Just as with $Co^{+2}$ the relaxation time can be interpreted only in terms of the presence of another aquo zinc ion in addition to $Zn(H_2O)_6^{+2}$. The similarity of $\tau$, $\Delta H^*$, and $\Delta S^*$ to those observed with $Co^{+2}$ is strong evidence for this species being tetrahedral $Zn(H_2O)_4^{+2}$.

Since the temperature-jump, pH indicator method was successful with $Zn^{+2}$, it was thought advisable to check the $Co^{+2}$ results by the same method. The resulting relaxation effect, although not as large as that observed with $Zn^{+2}$, was nevertheless in perfect agreement with the result obtained from the direct spectral change.

Due to the large decrease in optical density associated with the temperature dependence of the indicator p$K$, the rapid increase in optical density of $Co^{+2}$ solutions mentioned previously could not be observed for either $Co^{+2}$ or $Zn^{+2}$ with the temperature-jump, pH indicator method.

In the light of this conclusion the results have a strong bearing on the problems proposed above concerning the mechanism of ligand substitution. The large entropy observed for the tetrahedral–octahedral transition undoubtedly arises from the distortion necessary to change the tetrahedral structure to a structure suitably near the octahedral. Such a distortion places severe restrictions on the positions of all the ligands with respect to the internal coordinate system of the complex and would be expected to have a relatively low probability of occurrence. The result is that the conversion to the much more thermodynamically stable octahedral form is relatively slow.

One of the problems proposed concerned the probability of a rearrangement of ligands in a complex in order to increase the crystal field stabilization during the process of ligand substitution. It would seem that this process also would encounter a sizable entropy barrier and therefore it is very unlikely that the ligand substitution rate constants are affected by it in the series of ions previously mentioned. Finally the upper limit of the rate of an alternate ligand substitution mechanism such as discussed in the Introduction was measured for $Co^{+2}$ and $Zn^{+2}$, and it is much too slow to be a contributing factor in the observed substitution rates. Because of the presence of the entropy barrier to structural changes it is likely that such an alternate substitution mechanism would also be too slow to be observed with the other doubly charged ions of the first transition series.

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CONTRIBUTION FROM THE LAWRENCE RADIATION LABORATORY AND DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA

# The Crystal Structure of Manganese Dichloride Tetrahydrate[1]

BY ALLAN ZALKIN, J. D. FORRESTER, AND DAVID H. TEMPLETON

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The stable room temperature form of $MnCl_2 \cdot 4H_2O$ ($\alpha$ form) has a monoclinic cell, $a = 11.186$, $b = 9.513$, $c = 6.186$ Å., and $\beta = 99.74°$. The space group is $P2_1/n$ with four formula units per unit cell and $d_x = 2.03$ g./cc. An X-ray diffraction study of this material yielded the positions of all of the atoms including the hydrogens. The structure consists of discrete octahedra of four oxygen atoms and two chlorine atoms about the manganese, and with the chlorine atoms adjacent to each other. The four Mn–O distances are nearly equidistant, being 2.224, 2.209, 2.185, and 2.206 Å.; the two Mn–Cl distances are 2.475 and 2.500 Å. Only four of the eight hydrogen atoms make hydrogen bonds. Three of the hydrogen bonds are between oxygen and chlorine and one between two water molecules.

## Introduction

Groth[2] reports two monoclinic crystal modifications of $MnCl_2 \cdot 4H_2O$. One form is metastable at room temperature (Dawson and Williams[3]) and is isomorphous with $FeCl_2 \cdot 4H_2O$, the structure of which has been described by Penfold and Grigor[4] with comments on the proton sites by El Saffar and Murtz.[5] Our paper deals with the form that is stable at room temperature, and in keeping with the nomenclature of Dawson and Williams[3] we refer to this modification as the $\alpha$ form and to the metastable modification as the $\beta$ form. It should be noted here that Groth[2] in his publication has reversed the naming of these two forms from the above convention.

Delain[6] has reported the cell dimensions and space group of the $\alpha$ form, and Gardner[7] has reported some preliminary results on the proton sites. We became

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(1) Work done under the auspices of the U. S. Atomic Energy Commission.

(2) P. Groth, "Chemische Krystallographie," Vol. I, Wilhelm Engelmann, Leipzig, 1908.

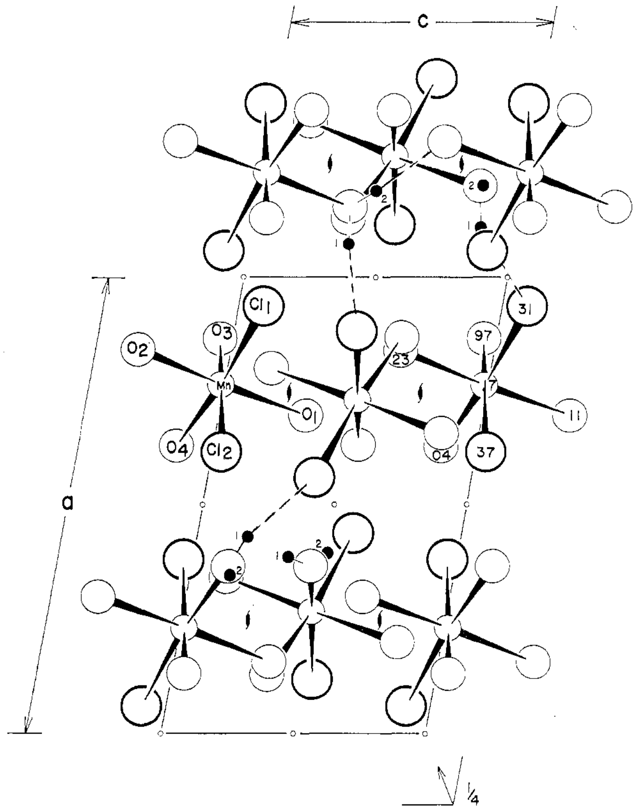
(3) H. M. Dawson and P. Williams, *Z. physik. Chem.*, **31**, 59 (1899).

(4) B. R. Penfold and J. A. Grigor, *Acta Cryst.*, **12**, 850 (1959).

(5) Z. M. El Saffar and C. R. K. Murtz, *ibid.*, **15**, 285 (1962).

(6) C. Delain, *Compt. rend.*, **238**, 1245 (1954).

(7) W. E. Gardner, *Bull. Am. Phys. Soc.*, **5**, 458 (1960).



$MnCl_2 \cdot 4H_2O$

Fig. 1.—Atomic arrangement of $MnCl_2 \cdot 4H_2O$. $y$ coordinates ($\times 100$) are indicated as numbers inside some of the circles. The small solid circles represent hydrogen atoms, and only one of each type is shown.

interested in the structure of this crystal after learning of its use as a sample for low temperature magnetic measurements by Professor W. F. Giauque.

## Experimental

An aqueous solution of manganous chloride was allowed to evaporate at room temperature and the tetrahydrate crystals grew readily in the form of approximately hexagonal plates. A suitable crystal with maximum dimension of 0.1 mm. was mounted and used for collecting the intensity data. Intensities were measured with a General Electric XRD-5 equipped with a goniostat, a scintillation counter, and a pulse height discriminator. Mo K$\alpha$ radiation was used and the unit cell dimensions are based on $\lambda = 0.70926$ Å. for Mo K$\alpha_1$. No preliminary X-ray photographs were taken; the crystal was aligned on the goniostat using the cell dimensions reported by Donnay,[8] together with the observations on the direction of extinction of polarized light. The systematic space group absences were carefully checked on the goniostat.

The 848 independent reflections permitted by the space group in the sphere with $\sin \theta/\lambda$ less than 0.538 ($2\theta$ less than 45°) were measured with counting times of 10 sec. each; of these, 49 were assigned zero intensity. The maximum intensity counted was 4200 counts/sec., which was the 002 reflection.

No corrections were made for either absorption or extinction. The absorption factor $\mu$ for this crystal with Mo radiation is 28 cm.$^{-1}$. $\mu R$ is about 0.14 or less, making the absorption very low.

Calculations were made with an IBM 7094 computer using a full matrix least-squares refinement program written by P. K. Gantzell, R. A. Sparks, and K. N. Trueblood with minor changes and Fourier and distance programs written by A. Zalkin. We minimized the function $\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2$.

Atomic scattering factors were taken as the values of Ibers[9] for $Mn^{+2}$, $Cl^-$, neutral O, and H. Dispersion corrections[10] of $-0.4$ and $-0.1$ electron were added to the $Mn^{+2}$ and $Cl^-$ scattering factors, respectively. The imaginary part of the dispersion correction was neglected.

TABLE I

FINAL POSITIONAL PARAMETERS AND STANDARD DEVIATIONS FOR $MnCl_2 \cdot 4H_2O$

| Atom | $x$ | $y$ | $z$ | $\sigma(x)$ | $\sigma(y)$ | $\sigma(z)$ |
|---|---|---|---|---|---|---|
| Mn | 0.2329 | 0.1714 | 0.9865 | 0.0001 | 0.0001 | 0.0001 |
| Cl(1) | 0.0610 | 0.3076 | 0.0938 | 0.0001 | 0.0001 | 0.0002 |
| Cl(2) | 0.3817 | 0.3662 | 0.0355 | 0.0001 | 0.0001 | 0.0002 |
| O(1) | 0.3010 | 0.1127 | 0.3334 | 0.0004 | 0.0005 | 0.0006 |
| O(2) | 0.1568 | 0.2280 | 0.6446 | 0.0004 | 0.0005 | 0.0007 |
| O(3) | 0.1323 | 0.9736 | 0.9590 | 0.0005 | 0.0006 | 0.0011 |
| O(4) | 0.3695 | 0.0381 | 0.8764 | 0.0004 | 0.0005 | 0.0007 |
| H(1)1[a] | 0.39 | 0.15 | 0.37 | 0.01 | 0.01 | 0.01 |
| H(1)2 | 0.30 | 0.02 | 0.35 | 0.01 | 0.01 | 0.01 |
| H(2)1 | 0.08 | 0.20 | 0.62 | 0.01 | 0.01 | 0.01 |
| H(2)2 | 0.19 | 0.21 | 0.56 | 0.01 | 0.01 | 0.02 |
| H(3)1 | 0.11 | 0.95 | 0.87 | 0.01 | 0.01 | 0.02 |
| H(3)2 | 0.10 | 0.99 | 0.01 | 0.02 | 0.02 | 0.03 |
| H(4)1 | 0.43 | 0.09 | 0.81 | 0.01 | 0.01 | 0.02 |
| H(4)2 | 0.35 | 0.95 | 0.86 | 0.01 | 0.01 | 0.01 |

[a] H($i$)$j$ means that it is the $j$th hydrogen of water oxygen O($i$).

## Results

**Unit Cell and Space Group.**—The primitive cell is monoclinic, contains four formula units ($MnCl_2 \cdot 4H_2O$) per unit cell, and has the dimensions: $a = 11.186 \pm 0.006$, $b = 9.513 \pm 0.005$, $c = 6.186 \pm 0.002$ Å., $\beta = 99.74 \pm 0.04°$, $V = 648.8$ Å.$^3$, $a{:}b{:}c = 1.1759{:}1{:}0.6503$. These compare with values $a = 11.3$, $b = 9.55$, $c = 6.15$ Å., and $\beta = 99.63°$ reported by Delain[6] (after transformation from $P2_1/a$) and the axial ratios of 1.1525:1:0.6445 with $\beta = 99.42°$ by Groth.[2]

From the X-ray data the calculated density is 2.03 g./cc., which compares with the value of 2.01 g./cc. reported in the literature.[11]

Reflections $h0l$ are absent unless $h + l = 2n$ and $0k0$ reflections are absent unless $k = 2n$. This is characteristic of the space group $P2_1/n$ ($C_{2h}^5$), and the success of our structure determination confirms this symmetry.

**Determination of the Structure.**—Projection data were collected initially and the Patterson functions for three projections $hk0$, $h0l$, and $0kl$ were calculated from the observed intensities after correction for Lorentz and polarization effects. From these three projections, the positions of the Mn and the two independent Cl atoms required by the four formula units per unit cell were obtained directly. These three atoms were all in 4-fold general positions: 4(e): $\pm(x, y, z;\ {}^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z)$.

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[8] J. D. H. Donnay, "Crystal Data," 2nd Ed., American Crystallographic Association Monograph, 1963 p. 161.

[9] J. A. Ibers, "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p. 210.

[10] D. H. Templeton, ref. 9, p. 215.

[11] "Handbook of Chemistry and Physics," 39th Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1957, p. 554.

TABLE II

THERMAL PARAMETERS[a] AND STANDARD DEVIATIONS

| Atom | $B_{11}$[b] | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|
| Mn | 1.98 ± 0.04 | 1.81 ± 0.04 | 1.50 ± 0.04 | −0.02 ± 0.03 | 0.36 ± 0.03 | 0.01 ± 0.03 |
| Cl(1) | 2.16 ± 0.06 | 2.76 ± 0.07 | 2.51 ± 0.06 | 0.43 ± 0.05 | 0.65 ± 0.05 | −0.29 ± 0.05 |
| Cl(2) | 2.22 ± 0.06 | 2.03 ± 0.06 | 2.38 ± 0.06 | −0.29 ± 0.05 | 0.35 ± 0.05 | 0.00 ± 0.05 |
| O(1) | 3.3 ± 0.2 | 2.2 ± 0.2 | 2.0 ± 0.2 | −0.1 ± 0.2 | 0.2 ± 0.1 | 0.1 ± 0.1 |
| O(2) | 2.5 ± 0.2 | 3.2 ± 0.2 | 2.2 ± 0.2 | −0.2 ± 0.2 | 0.5 ± 0.2 | 0.3 ± 0.2 |
| O(3) | 4.1 ± 0.2 | 3.1 ± 0.2 | 3.4 ± 0.3 | −1.2 ± 0.2 | 1.0 ± 0.2 | −0.6 ± 0.2 |
| O(4) | 3.5 ± 0.2 | 2.6 ± 0.2 | 3.7 ± 0.2 | 0.1 ± 0.2 | 1.5 ± 0.2 | −0.1 ± 0.2 |

| Atom | $B$[c] | Atom | $B$ | Atom | $B$ |
|---|---|---|---|---|---|
| H(1)1 | 2 ± 2 | H(2)2 | 5 ± 3 | H(4)1 | 6 ± 3 |
| H(1)2 | 3 ± 2 | H(3)1 | 6 ± 5 | H(4)2 | 5 ± 2 |
| H(2)1 | 1 ± 1 | H(3)2 | 21 ± 9 | | |

[a] Units are Å.$^2$. [b] The anisotropic values $B_{ij} = 4\beta_{ij}/a_i^*a_j^*$ where $a_i^*$ is the $i$th reciprocal cell length. [c] Isotropic.

When all of the three-dimensional data were available, a three-dimensional Fourier was calculated with phases based on the positions of the Mn and two Cl atoms. In this Fourier, all four independent oxygen atoms were found in general positions.

The parameters of these seven sets of atoms were refined by least squares using all the data, each with unit weight, and giving each atom an isotropic temperature factor of the form $\exp(-B\lambda^{-2}\sin^2\theta)$. After eight cycles of refinement, the conventional unreliability factor $R = \Sigma\,||F_o| - |F_c||/\Sigma|F_o|$ decreased to 0.083. Correction of several blunders in the data taking and in the card punching and the introduction of anisotropic temperature factors of the form $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)$ for each of the seven atoms reduced $R$ to 0.047 after four more cycles of refinement.

An electron density difference function with all atoms subtracted out with the exception of hydrogen was calculated using the results of this anisotropic refinement and using the terms for which $\sin\theta/\lambda < 0.48$. Eight out of the ten highest peaks in this function corresponded to reasonable positions for the eight independent hydrogen atoms in general positions. Four of these hydrogen atoms were suitably located to be hydrogen bonded.

Four cycles of least squares refinement with all eight hydrogen atoms each having isotropic temperature factors and the remaining seven heavier atoms having anisotropic temperature factors resulted in an $R$ factor of 0.041. The temperature factors of the four bonded hydrogen atoms remained normal, but those of two of the unbonded atoms, attached to O(3), had higher values. These temperature factors gave us concern that these atoms were misplaced, but a Fourier synthesis of $(F_o - F_c)$ gave no evidence of another position.

After four more cycles of refinement, the final $R$ value was 0.039. The final positional parameters and thermal parameters are listed in Tables I and II, respectively. The observed and calculated structure factors are listed in Table III.

Standard deviations of the parameters of the atoms were calculated assuming that the discrepancies in the structure factors represent random errors. The high standard deviations of the parameters of the hydrogen atoms illustrate that we are at the limit of our data's accuracy in determining these values.

**Description of the Structure.**—The structure consists of discrete octahedral groups with each manganese atom coordinated to two chlorine atoms at an average distance of 2.488 Å. and to four oxygen atoms at an average distance of 2.206 Å. Of the eight hydrogen atoms only four are involved in hydrogen bonding, which is discussed below. The over-all packing is illustrated in Fig. 1, and the dimensions of the octahedron are shown in Table IV. A complete list of distances less than 4.0 Å. is shown in Table V; the hydrogen atom distances are excluded.

The octahedron is only slightly distorted with the primary distortion due to the packing of the two larger chlorine atoms with the four somethat smaller oxygen atoms. The chlorine atoms are adjacent in each octahedron and not opposite as in the $FeCl_2 \cdot 4H_2O$ structure[4] although both structures have discrete octahedra. Also in the $FeCl_2 \cdot 4H_2O$ structure there are two different octahedral Fe–O distances (2.09 and 2.59 Å.), whereas in the $MnCl_2 \cdot 4H_2O$ all four Mn–O distances are almost equivalent (2.19 to 2.22 Å.). The densities of the two substances are very similar (2.03 g./cc. for the Mn compound, 1.98 g./cc. for the Fe compound), indicating that the efficiency of packing is also comparable. These comparisons suggest a rather interesting phase transformation if the metastable $\beta$ form of $MnCl_2 \cdot 4H_2O$ is indeed isomorphous with $FeCl_2 \cdot 4H_2O$ as is suggested by Groth.[2]

According to Groth[2] $MnBr_2 \cdot 4H_2O$ has axial cell ratios and $\beta$ angle very close to $MnCl_2 \cdot 4H_2O$ and is presumably isostructural with the structure described in this paper.

There is a similarity between the $MnCl_2 \cdot 4H_2O$ structure and that reported by Culot, *et al.*,[12] for $NaBr \cdot 2H_2O$. Dawson and Williams[3] remark that $MnCl_2 \cdot 4H_2O$ and $NaCl \cdot 2H_2O$ are isomorphous, and the relation is further expanded by Groth,[2] who states that $NaCl \cdot 2H_2O$ and $NaBr \cdot 2H_2O$ are isomorphous. If the monoclinic cell for $NaBr \cdot 2H_2O$ is doubled along its $a$ axis and a different setting chosen, the resulting cell has axial ratios and $\beta$ angle as follows: $a:b:c = 1.171:1:0.653$ with $\beta =$

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(12) J. P. Culot, P. Piret, and M. Van Meerssche, *Bull. Soc. Franc. Mineral. Cryst.*, **85**, 282 (1962).

TABLE III

OBSERVED STRUCTURE FACTOR MAGNITUDES × 5 (FOB) AND CALCULATED STRUCTURE FACTORS × 5 (FCA)

| H,K | L | FOB | FCA |
|---|---|---|---|
| 0, 0 | 2 | 694 | 696 |
| | 4 | 118 | 109 |
| | 6 | 133 | 138 |
| 0, 1 | 1 | 102 | 79 |
| | 2 | 260 | -270 |
| | 3 | 133 | 128 |
| | 4 | 110 | -112 |
| | 5 | 69 | 69 |
| | 6 | 45 | 49 |
| 0, 2 | 0 | 333 | -322 |
| | 1 | 140 | 136 |
| | 2 | 201 | -194 |
| | 3 | 291 | 287 |
| | 4 | 42 | -40 |
| | 5 | 179 | 175 |
| | 6 | 20 | -31 |
| 0, 3 | 1 | 225 | 236 |
| | 2 | 231 | 224 |
| | 3 | 255 | -253 |
| | 4 | 105 | -106 |
| | 5 | 216 | -212 |
| | 6 | 101 | -100 |
| 0, 4 | 0 | 196 | -191 |
| | 1 | 170 | -173 |
| | 2 | 193 | -191 |
| | 3 | 223 | -224 |
| | 4 | 168 | -177 |
| | 5 | 98 | -105 |
| | 6 | 76 | -77 |
| 0, 5 | 1 | 191 | 186 |
| | 2 | 15 | 15 |
| | 3 | 207 | 198 |
| | 4 | 40 | 43 |
| | 5 | 201 | 198 |
| 0, 6 | 0 | 356 | 350 |
| | 1 | 146 | 143 |
| | 2 | 338 | 328 |
| | 3 | 46 | 43 |
| | 4 | 174 | 169 |
| | 5 | 115 | -115 |
| 0, 7 | 1 | 29 | 34 |
| | 2 | 18 | -21 |
| | 3 | 26 | -37 |
| | 4 | 20 | 22 |
| 0, 8 | 0 | 85 | -82 |
| | 1 | 26 | 16 |
| | 2 | 76 | -77 |
| | 3 | 20 | 21 |
| | 4 | 0 | -9 |
| 0, 9 | 1 | 204 | -200 |
| | 2 | 29 | 33 |
| | 3 | 82 | -86 |
| 0,10 | 0 | 0 | -17 |
| | 1 | 0 | -6 |
| 1, 0 | -5 | 98 | -98 |
| | -3 | 49 | -49 |
| | -1 | 51 | 51 |
| | 1 | 88 | 81 |
| | 3 | 30 | 31 |
| | 5 | 65 | -63 |
| 1, 1 | -6 | 34 | -41 |
| | -5 | 150 | -150 |
| | -4 | 52 | 53 |
| | -3 | 360 | -355 |
| | -2 | 124 | -118 |
| | -1 | 452 | -433 |
| | 0 | 45 | 48 |
| | 1 | 497 | -482 |
| | 2 | 476 | 472 |
| | 3 | 471 | -470 |
| | 4 | 214 | 212 |
| | 5 | 120 | -118 |
| | 6 | 95 | 99 |
| 1, 2 | -6 | 88 | -88 |
| | -5 | 60 | 66 |
| | -4 | 105 | -98 |
| | -3 | 14 | -3 |
| | -2 | 26 | -7 |
| | -1 | 90 | -86 |
| | 0 | 258 | -252 |
| | 1 | 61 | -58 |
| | 2 | 98 | -93 |
| | 3 | 91 | 84 |
| | 4 | 94 | -87 |
| | 5 | 74 | 76 |
| | 6 | 197 | -199 |
| 1, 3 | -6 | 20 | 24 |
| | -5 | 49 | -42 |
| | -4 | 23 | 24 |
| | -3 | 69 | -63 |
| | -2 | 54 | 51 |
| | -1 | 34 | -36 |
| | 0 | 0 | 16 |
| | 1 | 11 | -17 |
| | 2 | 121 | -117 |
| | 3 | 59 | 56 |
| | 4 | 216 | -212 |
| | 5 | 62 | 62 |
| | 6 | 171 | -179 |
| 1, 4 | -6 | 101 | 105 |
| | -5 | 33 | 33 |
| | -4 | 289 | 292 |
| | -3 | 59 | 61 |
| | -2 | 437 | 431 |
| | -1 | 55 | -50 |
| | 0 | 207 | 214 |
| | 1 | 296 | 297 |
| | 2 | 99 | 91 |
| | 3 | 219 | 217 |
| | 4 | 143 | 139 |
| | 5 | 0 | 4 |
| 1, 5 | -5 | 188 | 186 |
| | -4 | 40 | -38 |
| | -3 | 322 | 316 |
| | -2 | 72 | -70 |
| | -1 | 398 | 388 |
| | 0 | 118 | -118 |
| | 1 | 319 | 309 |
| | 2 | 65 | -65 |
| | 3 | 201 | 200 |
| | 4 | 128 | 129 |
| | 5 | 75 | 74 |
| 1, 6 | -5 | 80 | -81 |
| | -4 | 144 | -141 |
| | -3 | 25 | -22 |
| | -2 | 168 | -161 |
| | -1 | 74 | 75 |
| | 0 | 88 | -88 |
| | 1 | 77 | 76 |
| | 2 | 16 | -15 |
| | 3 | 18 | 9 |
| | 4 | 27 | 29 |
| | 5 | 0 | 16 |
| 1, 7 | -4 | 0 | -20 |
| | -3 | 59 | 52 |
| | -2 | 53 | 46 |
| | -1 | 116 | -117 |
| | 0 | 140 | 143 |
| | 1 | 314 | -313 |
| | 2 | 162 | 163 |
| | 3 | 162 | -160 |
| | 4 | 64 | 63 |
| 1, 8 | -4 | 21 | -31 |
| | -3 | 20 | -20 |
| | -2 | 53 | -49 |
| | -1 | 108 | -111 |
| | 0 | 65 | -63 |
| | 1 | 166 | -164 |
| | 2 | 126 | -126 |
| | 3 | 78 | -78 |
| 1, 9 | -3 | 76 | -76 |
| | -2 | 29 | 31 |
| | -1 | 34 | -26 |
| | 0 | 34 | 28 |
| | 1 | 63 | 59 |
| | 2 | 0 | -14 |
| 1,10 | -1 | 99 | 112 |
| | 0 | 120 | 130 |
| | 1 | 42 | 48 |
| 2, 0 | -6 | 403 | -407 |
| | -4 | 423 | -423 |
| | -2 | 54 | 62 |
| | 0 | 367 | -355 |
| | 2 | 480 | -471 |
| | 4 | 81 | -77 |
| | 6 | 29 | -39 |
| 2, 1 | -6 | 82 | 89 |
| | -5 | 43 | -37 |
| | -4 | 241 | 236 |
| | -3 | 192 | -192 |
| | -2 | 255 | 257 |
| | -1 | 240 | -235 |
| | 0 | 70 | -68 |
| | 1 | 211 | -204 |
| | 2 | 169 | -158 |
| | 3 | 192 | -182 |
| | 4 | 16 | -13 |
| | 5 | 69 | -63 |
| | 6 | 21 | -23 |
| 2, 2 | -6 | 126 | 130 |
| | -5 | 70 | -71 |
| | -4 | 103 | 103 |
| | -3 | 199 | -198 |
| | -2 | 0 | 4 |
| | -1 | 277 | -286 |
| | 0 | 85 | 68 |
| | 1 | 33 | -35 |
| | 2 | 249 | 246 |
| | 3 | 144 | -139 |
| | 4 | 197 | 194 |
| | 5 | 189 | -187 |
| | 6 | 69 | 83 |
| 2, 3 | -6 | 29 | 26 |
| | -5 | 26 | -11 |
| | -4 | 120 | -118 |
| | -3 | 329 | 320 |
| | -2 | 144 | 136 |
| | -1 | 585 | 582 |
| | 0 | 483 | 508 |
| | 1 | 288 | 287 |
| | 2 | 90 | 90 |
| | 3 | 239 | 231 |
| | 4 | 24 | 25 |
| | 5 | 193 | 189 |
| 2, 4 | -6 | 70 | 36 |
| | -5 | 60 | 58 |
| | -4 | 127 | 128 |
| | -3 | 150 | 150 |
| | -2 | 202 | 195 |
| | -1 | 77 | 71 |
| | 0 | 154 | 152 |
| | 1 | 44 | 38 |
| | 2 | 38 | -33 |
| | 3 | 77 | 76 |
| | 4 | 25 | -18 |
| | 5 | 123 | 123 |
| 2, 5 | -5 | 117 | -118 |
| | -4 | 92 | -83 |
| | -3 | 242 | -235 |
| | -2 | 102 | -101 |
| | -1 | 347 | -346 |
| | 0 | 14 | -22 |
| | 1 | 184 | -187 |
| | 2 | 72 | 71 |
| | 3 | 66 | 61 |
| | 4 | 32 | 30 |
| | 5 | 29 | 28 |
| 2, 6 | -5 | 36 | -33 |
| | -4 | 191 | -190 |
| | -3 | 39 | -37 |
| | -2 | 233 | -223 |
| | -1 | 303 | 305 |
| | 0 | 146 | -142 |
| | 1 | 283 | 290 |
| | 2 | 164 | -163 |
| | 3 | 57 | 52 |
| | 4 | 168 | -168 |
| | 5 | 0 | 3 |
| 2, 7 | -4 | 53 | 59 |
| | -3 | 26 | 20 |
| | -2 | 18 | -4 |
| | -1 | 17 | 19 |
| | 0 | 79 | -79 |
| | 1 | 86 | -89 |
| | 2 | 130 | -130 |
| | 3 | 144 | -143 |
| | 4 | 125 | -115 |
| 2, 8 | -4 | 36 | 34 |
| | -3 | 0 | -6 |
| | -2 | 27 | 27 |
| | -1 | 18 | -15 |
| | 0 | 26 | 35 |
| | 1 | 62 | -69 |
| | 2 | 178 | 178 |
| | 3 | 70 | -68 |
| 2, 9 | -3 | 112 | 107 |
| | -2 | 73 | 68 |
| | -1 | 131 | 132 |
| | 0 | 183 | 191 |
| | 1 | 194 | 190 |
| | 2 | 165 | 162 |
| 2,10 | -1 | 21 | -32 |
| | 0 | 56 | 56 |
| 3, 0 | -5 | 83 | 83 |
| | -3 | 131 | 133 |
| | -1 | 150 | 160 |
| | 1 | 70 | 71 |
| | 3 | 296 | -305 |
| | 5 | 265 | -264 |
| 3, 1 | -6 | 20 | 5 |
| | -5 | 216 | 220 |
| | -4 | 218 | -218 |
| | -3 | 374 | 367 |
| | -2 | 401 | -401 |
| | -1 | 227 | 209 |
| | 0 | 133 | -140 |
| | 1 | 206 | -216 |
| | 2 | 104 | -99 |
| | 3 | 56 | 54 |
| | 4 | 29 | -27 |
| | 5 | 157 | 155 |
| | 6 | 0 | 2 |
| 3, 2 | -6 | 67 | 76 |
| | -5 | 0 | -23 |
| | -4 | 167 | 164 |
| | -3 | 150 | -153 |
| | -2 | 226 | 222 |
| | -1 | 292 | -295 |
| | 0 | 625 | 668 |
| | 1 | 52 | 53 |
| | 2 | 595 | 595 |
| | 3 | 220 | 216 |
| | 4 | 195 | 194 |
| | 5 | 100 | 99 |
| 3, 3 | -6 | 21 | -19 |
| | -5 | 37 | -34 |
| | -4 | 80 | 84 |
| | -3 | 70 | -68 |
| | -2 | 206 | 213 |
| | -1 | 140 | -140 |
| | 0 | 275 | 282 |
| | 1 | 26 | -30 |
| | 2 | 103 | 101 |
| | 3 | 16 | 26 |
| | 4 | 18 | -18 |
| | 5 | 98 | -93 |
| 3, 4 | -6 | 79 | -75 |
| | -5 | 121 | -118 |
| | -4 | 81 | -83 |
| | -3 | 281 | -277 |
| | -2 | 293 | -286 |
| | -1 | 36 | -44 |
| | 0 | 430 | -443 |
| | 1 | 28 | 27 |
| | 2 | 298 | -299 |
| | 3 | 44 | -43 |
| | 4 | 107 | -102 |
| | 5 | 83 | 84 |
| 3, 5 | -5 | 151 | -154 |
| | -4 | 36 | 38 |
| | -3 | 161 | -158 |
| | -2 | 129 | -130 |
| | -1 | 103 | -101 |
| | 0 | 167 | -167 |
| | 1 | 0 | -2 |
| | 2 | 74 | 70 |
| | 3 | 18 | 6 |
| | 4 | 27 | 19 |
| | 5 | 0 | -12 |
| 3, 6 | -5 | 29 | 26 |
| | -4 | 27 | -27 |
| | -3 | 64 | 60 |
| | -2 | 37 | -38 |
| | -1 | 28 | 21 |
| | 0 | 0 | -9 |
| | 1 | 111 | -118 |
| | 2 | 65 | 57 |
| | 3 | 144 | -140 |
| | 4 | 35 | -35 |
| 3, 7 | -4 | 98 | -97 |
| | -3 | 192 | 182 |
| | -2 | 60 | -60 |
| | -1 | 98 | 96 |
| | 0 | 30 | -27 |
| | 1 | 198 | 205 |
| | 2 | 86 | -90 |
| | 3 | 180 | 177 |
| | 4 | 59 | -53 |
| 3, 8 | -4 | 102 | 106 |
| | -3 | 28 | 32 |
| | -2 | 168 | 166 |
| | -1 | 19 | 1 |
| | 0 | 128 | 127 |
| | 1 | 102 | 98 |
| | 2 | 132 | 132 |
| | 3 | 132 | 130 |
| 3, 9 | -2 | 29 | 25 |
| | -1 | 53 | -57 |
| | 0 | 20 | 17 |
| | 1 | 20 | -26 |
| | 2 | 21 | 22 |
| 4, 0 | -6 | 94 | 98 |
| | -4 | 359 | 355 |
| | -2 | 109 | 105 |
| | 0 | 171 | -181 |
| | 2 | 24 | 17 |
| | 4 | 0 | -5 |
| 4, 1 | -6 | 0 | 6 |
| | -5 | 106 | 108 |
| | -4 | 51 | 49 |
| | -3 | 194 | 191 |
| | -2 | 80 | -81 |
| | -1 | 157 | 156 |
| | 0 | 40 | -47 |
| | 1 | 78 | 85 |
| | 2 | 218 | 212 |
| | 3 | 204 | 203 |
| | 4 | 229 | 231 |
| | 5 | 88 | 88 |
| 4, 2 | -6 | 50 | -49 |
| | -5 | 0 | -2 |
| | -4 | 187 | -186 |
| | -3 | 44 | 41 |
| | -2 | 316 | -318 |
| | -1 | 299 | 299 |
| | 0 | 255 | -260 |
| | 1 | 134 | 136 |
| | 2 | 95 | -93 |
| | 3 | 42 | -40 |
| | 4 | 31 | -29 |
| | 5 | 0 | 5 |
| 4, 3 | -6 | 134 | -134 |
| | -5 | 166 | -165 |
| | -4 | 68 | -74 |
| | -3 | 227 | -219 |
| | -2 | 78 | 76 |
| | -1 | 528 | -530 |
| | 0 | 47 | -43 |
| | 1 | 512 | -526 |
| | 2 | 42 | 43 |
| | 3 | 333 | -326 |
| | 4 | 58 | 59 |
| | 5 | 147 | -144 |
| 4, 4 | -6 | 30 | -40 |
| | -5 | 51 | 50 |
| | -4 | 31 | 23 |
| | -3 | 60 | -59 |
| | -2 | 45 | 47 |
| | -1 | 188 | -183 |
| | 0 | 87 | -86 |
| | 1 | 219 | -227 |
| | 2 | 16 | -5 |
| | 3 | 108 | -105 |
| | 4 | 19 | 29 |
| | 5 | 0 | 4 |
| 4, 5 | -5 | 72 | 77 |
| | -4 | 26 | -6 |
| | -3 | 57 | -54 |
| | -2 | 23 | -18 |
| | -1 | 60 | -60 |
| | 0 | 40 | -35 |
| | 1 | 131 | 133 |
| | 2 | 163 | -168 |
| | 3 | 104 | 108 |
| | 4 | 170 | -171 |
| 4, 6 | -5 | 164 | -162 |
| | -4 | 138 | 144 |
| | -3 | 0 | -11 |
| | -2 | 221 | 225 |
| | -1 | 70 | 68 |
| | 0 | 138 | 136 |
| | 1 | 70 | 68 |
| | 2 | 36 | 25 |
| | 3 | 108 | 104 |
| | 4 | 65 | 65 |
| 4, 7 | -4 | 41 | 44 |
| | -3 | 172 | 173 |
| | -2 | 48 | 49 |
| | -1 | 166 | 163 |
| | 0 | 0 | -4 |
| | 1 | 103 | 99 |
| | 2 | 0 | -9 |
| | 3 | 57 | 57 |
| 4, 8 | -3 | 41 | 39 |
| | -2 | 285 | -291 |
| | -1 | 27 | 15 |
| | 0 | 178 | -187 |
| | 1 | 19 | 17 |
| | 2 | 60 | -61 |
| | 3 | 42 | 42 |
| 4, 9 | -2 | 0 | -6 |
| | -1 | 54 | -58 |
| | 0 | 68 | 66 |
| | 1 | 111 | -117 |
| 5, 0 | -5 | 18 | 34 |
| | -3 | 261 | 260 |
| | -1 | 467 | 480 |
| | 1 | 90 | 95 |
| | 3 | 37 | 41 |
| | 5 | 216 | 227 |
| 5, 1 | -6 | 0 | 6 |
| | -5 | 0 | 20 |
| | -4 | 17 | -21 |
| | -3 | 111 | -106 |
| | -2 | 24 | 24 |
| | -1 | 440 | -452 |
| | 0 | 68 | -73 |
| | 1 | 243 | -251 |
| | 2 | 33 | -34 |
| | 3 | 47 | -46 |
| | 4 | 0 | -8 |
| | 5 | 54 | -55 |
| 5, 2 | -6 | 225 | -234 |
| | -5 | 27 | -22 |
| | -4 | 390 | -392 |
| | -3 | 183 | -179 |
| | -2 | 274 | -272 |
| | -1 | 112 | -115 |
| | 0 | 178 | -180 |
| | 1 | 14 | -4 |
| | 2 | 224 | -224 |
| | 3 | 88 | -86 |
| | 4 | 107 | -108 |
| | 5 | 118 | -109 |
| 5, 3 | -6 | 0 | -16 |
| | -5 | 38 | 33 |
| | -4 | 46 | 43 |
| | -3 | 0 | 5 |
| | -2 | 111 | 110 |
| | -1 | 126 | 127 |
| | 0 | 72 | -64 |
| | 1 | 180 | 183 |
| | 2 | 249 | -253 |
| | 3 | 67 | -64 |
| | 4 | 113 | -115 |
| | 5 | 69 | -72 |
| 5, 4 | -5 | 44 | -37 |
| | -4 | 206 | 206 |
| | -3 | 24 | 26 |
| | -2 | 98 | 93 |
| | -1 | 104 | -103 |
| | 0 | 54 | 53 |
| | 1 | 290 | -302 |
| | 2 | 142 | 142 |
| | 3 | 183 | -177 |
| | 4 | 156 | 157 |
| 5, 5 | -5 | 0 | 22 |
| | -4 | 68 | -66 |
| | -3 | 35 | 33 |
| | -2 | 55 | -50 |
| | -1 | 68 | 64 |
| | 0 | 204 | 205 |
| | 1 | 101 | 101 |
| | 2 | 208 | 204 |
| | 3 | 103 | 100 |
| | 4 | 109 | 101 |
| 5, 6 | -5 | 56 | 54 |
| | -4 | 0 | -11 |
| | -3 | 122 | 120 |
| | -2 | 35 | 31 |
| | -1 | 94 | 92 |
| | 0 | 146 | 146 |
| | 1 | 88 | 89 |
| | 2 | 0 | 12 |
| | 3 | 100 | 98 |
| | 4 | 137 | -129 |
| 5, 7 | -4 | 36 | 37 |
| | -3 | 262 | -254 |
| | -2 | 38 | 34 |
| | -1 | 237 | -239 |
| | 0 | 94 | -94 |
| | 1 | 187 | -198 |
| | 2 | 120 | -123 |
| | 3 | 83 | -85 |
| 5, 8 | -3 | 85 | -89 |
| | -2 | 179 | -184 |
| | -1 | 0 | -3 |
| | 0 | 153 | -154 |
| | 1 | 72 | 71 |
| | 2 | 55 | -58 |
| 5, 9 | -2 | 67 | -68 |
| | -1 | 130 | 129 |
| | 0 | 118 | -119 |
| | 1 | 87 | 91 |
| 6, 0 | -6 | 0 | 20 |
| | -4 | 46 | -44 |
| | -2 | 160 | -156 |
| | 0 | 253 | -262 |
| | 2 | 380 | -382 |
| | 4 | 205 | -211 |
| 6, 1 | -6 | 29 | 30 |
| | -5 | 100 | -93 |
| | -4 | 142 | -142 |
| | -3 | 159 | -159 |
| | -2 | 340 | -337 |
| | -1 | 165 | -162 |
| | 0 | 340 | -347 |
| | 1 | 71 | 77 |
| | 2 | 248 | -244 |
| | 3 | 30 | 34 |
| | 4 | 77 | -76 |
| | 5 | 30 | -35 |
| 6, 2 | -6 | 60 | 68 |
| | -5 | 19 | -12 |
| | -4 | 58 | 61 |
| | -3 | 150 | 142 |
| | -2 | 97 | 97 |
| | -1 | 77 | 81 |
| | 0 | 161 | 172 |
| | 1 | 55 | -53 |
| | 2 | 190 | 189 |
| | 3 | 67 | -69 |
| | 4 | 70 | 70 |
| 6, 3 | -5 | 294 | 301 |
| | -4 | 18 | -8 |
| | -3 | 317 | 310 |
| | -2 | 106 | -102 |
| | -1 | 213 | 214 |
| | 0 | 46 | -47 |
| | 1 | 35 | 37 |
| | 2 | 34 | -37 |
| | 3 | 26 | -27 |
| | 4 | 63 | -66 |
| 6, 4 | -5 | 60 | 60 |
| | -4 | 62 | 53 |
| | -3 | 17 | 16 |
| | -2 | 16 | 12 |
| | -1 | 83 | -82 |
| | 0 | 134 | 136 |
| | 1 | 0 | 9 |
| | 2 | 158 | 155 |
| | 3 | 181 | 182 |
| | 4 | 46 | 51 |
| 6, 5 | -5 | 93 | -108 |
| | -4 | 118 | 116 |
| | -3 | 149 | -153 |
| | -2 | 214 | 211 |
| | -1 | 61 | -62 |
| | 0 | 148 | 149 |
| | 1 | 49 | -45 |
| | 2 | 111 | 119 |
| | 3 | 52 | -49 |
| | 4 | 103 | 104 |
| 6, 6 | -4 | 40 | -46 |
| | -3 | 76 | -74 |
| | -2 | 132 | -127 |
| | -1 | 100 | -103 |
| | 0 | 224 | -228 |
| | 1 | 88 | -91 |
| | 2 | 164 | -168 |
| | 3 | 132 | -122 |
| 6, 7 | -4 | 0 | 11 |
| | -3 | 40 | -38 |
| | -2 | 108 | -110 |
| | -1 | 33 | -33 |
| | 0 | 189 | -189 |
| | 1 | 34 | -25 |
| | 2 | 45 | -41 |
| 6, 8 | -3 | 0 | -7 |
| | -2 | 87 | 84 |
| | -1 | 49 | -52 |
| | 0 | 116 | 121 |
| | 1 | 77 | -71 |
| 7, 0 | -5 | 34 | -37 |
| | -3 | 0 | 8 |
| | -1 | 330 | -331 |
| | 1 | 388 | -392 |
| | 3 | 66 | -75 |
| 7, 1 | -5 | 171 | 167 |
| | -4 | 54 | 49 |
| | -3 | 63 | 61 |
| | -2 | 55 | 57 |
| | -1 | 163 | 165 |
| | 0 | 53 | 52 |
| | 1 | 274 | 276 |
| | 2 | 38 | -40 |
| | 3 | 216 | 211 |
| | 4 | 96 | -95 |
| 7, 2 | -5 | 28 | -34 |
| | -4 | 182 | 176 |
| | -3 | 61 | 68 |
| | -2 | 182 | 183 |
| | -1 | 220 | 224 |
| | 0 | 27 | 29 |
| | 1 | 161 | 165 |
| | 2 | 52 | -49 |
| | 3 | 80 | 81 |
| | 4 | 81 | -78 |
| 7, 3 | -5 | 64 | -64 |
| | -4 | 131 | 125 |
| | -3 | 68 | 66 |
| | -2 | 113 | 109 |
| | -1 | 169 | 174 |
| | 0 | 36 | -27 |
| | 1 | 17 | -16 |
| | 2 | 96 | 91 |
| | 3 | 19 | -24 |
| | 4 | 189 | 189 |
| 7, 4 | -5 | 145 | 142 |
| | -4 | 161 | -159 |
| | -3 | 188 | 180 |
| | -2 | 241 | -238 |
| | -1 | 107 | 110 |
| | 0 | 144 | -146 |
| | 1 | 98 | 99 |
| | 2 | 18 | -19 |
| | 3 | 39 | 39 |
| | 4 | 0 | -3 |
| 7, 5 | -4 | 159 | -155 |
| | -3 | 127 | -130 |
| | -2 | 44 | -48 |
| | -1 | 160 | -161 |
| | 0 | 18 | -21 |
| | 1 | 173 | -174 |
| | 2 | 38 | -36 |
| | 3 | 178 | -170 |
| 7, 6 | -4 | 29 | 27 |
| | -3 | 66 | -76 |
| | -2 | 200 | 205 |
| | -1 | 120 | -124 |
| | 0 | 151 | 150 |
| | 1 | 145 | -147 |
| | 2 | 0 | -6 |
| | 3 | 127 | -123 |
| 7, 7 | -3 | 85 | 84 |
| | -2 | 45 | 44 |
| | -1 | 40 | 36 |
| | 0 | 20 | -35 |
| | 1 | 50 | 48 |
| | 2 | 47 | -48 |
| 7, 8 | -2 | 42 | 43 |
| | -1 | 36 | 40 |
| | 0 | 30 | 43 |
| 8, 0 | -4 | 287 | 290 |
| | -2 | 315 | 316 |
| | 0 | 168 | 168 |
| | 2 | 131 | 134 |
| | 4 | 121 | 126 |
| 8, 1 | -5 | 29 | -22 |
| | -4 | 78 | 76 |
| | -3 | 35 | -34 |
| | -2 | 48 | 44 |
| | -1 | 125 | 127 |
| | 0 | 53 | 44 |
| | 1 | 71 | 73 |
| | 2 | 173 | 170 |
| | 3 | 19 | -21 |
| | 4 | 133 | 132 |
| 8, 2 | -5 | 35 | 39 |
| | -4 | 154 | -151 |
| | -3 | 98 | 97 |
| | -2 | 82 | -81 |
| | -1 | 171 | 174 |
| | 0 | 70 | 67 |
| | 1 | 209 | 206 |
| | 2 | 32 | 29 |
| | 3 | 108 | 111 |
| 8, 3 | -5 | 29 | -32 |
| | -4 | 28 | 22 |
| | -3 | 37 | -31 |
| | -2 | 68 | 65 |
| | -1 | 83 | -84 |
| | 0 | 0 | 8 |
| | 1 | 86 | -87 |
| | 2 | 89 | -92 |
| | 3 | 20 | -9 |
| 8, 4 | -4 | 153 | -147 |
| | -3 | 176 | -172 |
| | -2 | 100 | -98 |
| | -1 | 202 | -210 |
| | 0 | 95 | -92 |
| | 1 | 64 | -66 |
| | 2 | 140 | -137 |
| | 3 | 51 | -43 |
| 8, 5 | -4 | 36 | -35 |
| | -3 | 108 | 105 |
| | -2 | 83 | -81 |
| | -1 | 191 | 186 |
| | 0 | 73 | -72 |
| | 1 | 204 | 207 |
| | 2 | 35 | -33 |
| 8, 6 | -3 | 98 | 97 |
| | -2 | 116 | 113 |
| | -1 | 85 | 82 |
| | 0 | 94 | 98 |
| | 1 | 45 | -39 |
| | 2 | 73 | 78 |
| 8, 7 | -2 | 21 | -18 |
| | 0 | 135 | 137 |
| | 1 | 79 | -81 |
| 9, 0 | -5 | 170 | 171 |
| | -3 | 19 | -7 |
| 8, 7 | -1 | 41 | -48 |
| 9, 0 | -1 | 103 | -100 |
| | 3 | 89 | 91 |
| 9, 1 | -5 | 202 | -212 |
| | -4 | 34 | 36 |
| | -3 | 253 | -248 |
| | -2 | 124 | 127 |
| | -1 | 164 | -157 |
| | 0 | 165 | 158 |
| | 1 | 32 | -35 |
| | 2 | 150 | 147 |
| | 3 | 46 | 35 |
| 9, 2 | -5 | 88 | -86 |
| | -4 | 40 | 36 |
| | -3 | 38 | -34 |
| | -2 | 36 | 29 |
| | -1 | 25 | -23 |
| | 0 | 40 | -41 |
| | 1 | 32 | -22 |
| | 2 | 122 | -122 |
| | 3 | 42 | -48 |
| 9, 3 | -4 | 64 | -70 |
| | -3 | 61 | 61 |
| | -2 | 280 | -278 |
| | -1 | 45 | -49 |
| | 0 | 287 | -278 |
| | 1 | 38 | -37 |
| | 2 | 169 | -166 |
| | 3 | 30 | 25 |
| 9, 4 | -4 | 21 | 22 |
| | -3 | 20 | -15 |
| | -2 | 58 | 53 |
| | -1 | 33 | 27 |
| | 0 | 113 | 118 |
| | 1 | 44 | 39 |
| | 2 | 130 | 117 |
| 9, 5 | -3 | 183 | 181 |
| | -2 | 75 | 75 |
| | -1 | 153 | 153 |
| | 0 | 119 | 111 |
| | 1 | 29 | 37 |
| | 2 | 70 | 65 |
| 9, 6 | -2 | 0 | -2 |
| | -1 | 35 | 42 |
| | 0 | 88 | -85 |
| | 1 | 37 | 48 |
| 10, 0 | -4 | 127 | -128 |
| | -2 | 208 | -202 |
| | 0 | 129 | -130 |
| | 2 | 29 | 34 |
| 10, 1 | -4 | 97 | -101 |
| | -3 | 0 | 2 |
| | -2 | 121 | -126 |
| | -1 | 33 | -29 |
| | 0 | 19 | 21 |
| | 1 | 92 | -88 |
| | 2 | 35 | 28 |
| 10, 2 | -4 | 0 | 10 |
| | -3 | 116 | -119 |
| | -2 | 125 | 121 |
| | -1 | 172 | -170 |
| | 0 | 104 | 102 |
| | 1 | 252 | -251 |
| | 2 | 21 | -27 |
| 10, 3 | -4 | 82 | 77 |
| | -3 | 29 | 36 |
| | -2 | 97 | 101 |
| | -1 | 19 | 11 |
| | 0 | 52 | 46 |
| | 1 | 70 | 69 |
| | 2 | 0 | 11 |
| 10, 4 | -3 | 0 | 15 |
| | -2 | 40 | 40 |
| | -1 | 164 | 160 |
| | 0 | 70 | -66 |
| | 1 | 218 | 213 |
| 10, 5 | -2 | 0 | 10 |
| | -1 | 55 | 53 |
| | 0 | 42 | 40 |
| 11, 0 | -3 | 146 | -142 |
| | -1 | 123 | -124 |
| | 1 | 137 | -134 |
| 11, 1 | -3 | 0 | -4 |
| | -2 | 114 | -105 |
| | -1 | 20 | 23 |
| | 0 | 73 | -69 |
| | 1 | 46 | 43 |
| 11, 2 | -3 | 55 | 55 |
| | -2 | 124 | 121 |
| | -1 | 101 | 93 |
| | 0 | 54 | 53 |
| | 1 | 79 | 77 |
| 11, 3 | -2 | 72 | 74 |
| | -1 | 55 | -57 |
| | 0 | 108 | 107 |
| 11, 4 | -1 | 0 | -16 |

97.3°; this is quite similar to the values for $MnCl_2 \cdot 4H_2O$ reported here. The $NaBr \cdot 2H_2O$ structure also consists of octahedra with the halide atoms adjacent. These octahedra, however, each share an edge with each of three adjacent octahedra, consistent with one extra cation in the formula ($Na_2Br_2 \cdot 4H_2O$ as opposed to $MnCl_2 \cdot 4H_2O$) and form sheets in contrast with discrete octahedra in $MnCl_2 \cdot 4H_2O$.

**Hydrogen Bonding.**—All eight independent H atoms were located from the difference function calculated after an anisotropic refinement of the seven heavier atoms. Four of these are in a suitable environment to participate in hydrogen bonding, but the other four have no close neighbors that would indicate such bonding. A representative of each independent H atom is shown in Fig. 1 and appropriate distances for the four

TABLE IV

DIMENSIONS OF THE OCTAHEDRON AROUND MANGANESE IN $MnCl_2 \cdot 4H_2O$

| Atoms | Distance, Å. |
|---|---|
| Mn–Cl(1) | 2.500 ± 0.002 (2.506)[a] |
| Mn–Cl(2) | 2.475 ± 0.002 (2.478) |
| Mn–O(1) | 2.224 ± 0.004 (2.229) |
| Mn–O(2) | 2.209 ± 0.004 (2.215) |
| Mn–O(3) | 2.185 ± 0.006 (2.198) |
| Mn–O(4) | 2.206 ± 0.005 (2.216) |

| Atoms | Angles | Atoms | Angles |
|---|---|---|---|
| Cl(1)–Mn–Cl(2) | 96° | O(1)–Mn–O(2) | 177° |
| Cl(1)–Mn–O(1) | 92° | O(1)–Mn–O(3) | 87° |
| Cl(1)–Mn–O(2) | 87° | O(1)–Mn–O(4) | 92° |
| Cl(1)–Mn–O(3) | 93° | O(2)–Mn–O(3) | 92° |
| Cl(1)–Mn–O(4) | 174° | O(2)–Mn–O(4) | 90° |
| Cl(2)–Mn–O(1) | 88° | O(3)–Mn–O(4) | 82° |
| Cl(2)–Mn–O(2) | 94° | | |
| Cl(2)–Mn–O(3) | 169° | | |
| Cl(2)–Mn–O(4) | 89° | | |

[a] Distances in parentheses are values corrected for thermal motion assuming that the O and Cl atoms "ride" on the Mn.

bonded hydrogens are indicated in Table V. The four hydrogen bonds are as given below.

| | |
|---|---|
| O(1)—H(1)1 ············ Cl(1) | 3.17 Å. |
| O(2)—H(2)1 ············ Cl(2) | 3.17 Å. |
| O(2)—H(2)2 ············ O(1) | 2.93 Å. |
| O(4)—H(4)1 ············ Cl(1) | 3.29 Å. |

All of the distances above represent hydrogen bonding between atoms in different octahedra.

TABLE V

DISTANCES UNDER 4.0 Å. WITH STANDARD DEVIATIONS IN $MnCl_2 \cdot 4H_2O$[a]

| Atom | Distance, Å. | Atom | Distance, Å. |
|---|---|---|---|
| Cl(1)–Mn | 2.500 ± 0.002 | O(2)–Mn | 2.209 ± 0.004 |
| Cl(1)–O(2) | 3.233 ± 0.005[b] | O(2)–O(4) | 3.117 ± 0.007[b] |
| Cl(1)–O(1) | 3.391 ± 0.005[b] | O(2)–O(3) | 3.146 ± 0.008[b] |
| Cl(1)–O(3) | 3.414 ± 0.006[b] | O(2)–Cl(1) | 3.233 ± 0.005[b] |
| Cl(1)–Cl(2) | 3.708 ± 0.003[b] | O(2)–Cl(2) | 3.442 ± 0.005[b] |
| Cl(1)–O(1) | 3.169 ± 0.005[c] | O(2)–O(1) | 2.926 ± 0.006[c] |
| Cl(1)–O(4) | 3.292 ± 0.005[c] | O(2)–Cl(2) | 3.166 ± 0.005[c] |
| Cl(1)–O(2) | 3.477 ± 0.005 | O(2)–Cl(1) | 3.477 ± 0.005 |
| Cl(2)–Mn | 2.475 ± 0.002 | O(3)–Mn | 2.185 ± 0.006 |
| Cl(2)–O(1) | 3.254 ± 0.005[b] | O(3)–O(4) | 2.872 ± 0.008[b] |
| Cl(2)–O(4) | 3.285 ± 0.005[b] | O(3)–O(1) | 3.033 ± 0.008[b] |
| Cl(2)–O(2) | 3.442 ± 0.005[b] | O(3)–O(2) | 3.146 ± 0.008[b] |
| Cl(2)–Cl(1) | 3.708 ± 0.003[b] | O(3)–Cl(1) | 3.414 ± 0.006[b] |
| Cl(2)–O(2) | 3.166 ± 0.005[c] | O(3)–Cl(2) | 3.815 ± 0.007 |
| Cl(2)–O(3) | 3.815 ± 0.007 | O(4)–Mn | 2.206 ± 0.005 |
| O(1)–Mn | 2.224 ± 0.004 | O(4)–O(3) | 2.872 ± 0.008[b] |
| O(1)–O(3) | 3.033 ± 0.008[b] | O(4)–O(2) | 3.117 ± 0.007[b] |
| O(1)–O(4) | 3.185 ± 0.006[b] | O(4)–O(1) | 3.185 ± 0.006[b] |
| O(1)–Cl(2) | 3.254 ± 0.005[b] | O(4)–Cl(2) | 3.285 ± 0.005[b] |
| O(1)–Cl(1) | 3.391 ± 0.005[b] | O(4)–Cl(1) | 3.292 ± 0.005[c] |
| O(1)–O(2) | 2.926 ± 0.006[c] | O(4)–O(1) | 3.339 ± 0.006 |
| O(1)–Cl(1) | 3.169 ± 0.005[c] | | |
| O(1)–O(4) | 3.339 ± 0.006 | | |

[a] Hydrogen atom distances are not included. [b] Octahedral edge. [c] Hydrogen bond.

The distances calculated for the O–H distances in water from the parameters listed in Table I are 0.8 and 1.0 Å. for O(1); 0.8 and 0.9 Å. for O(2); 0.5 and 0.6 Å. for O(3); and 0.9 and 1.0 Å. for O(4). It is because of the limited accuracy of our hydrogen parameters that we have not presented a detailed list of distances to the hydrogen atoms.

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# Ion Exchange in Mixed Solvents. I. Monovalent Cations on a Strong Acid Exchanger[1]

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The ion-exchange behavior of $Li^+$, $Na^+$, and $K^+$ on Amberlite CG-120 Type 1 (strong acid exchanger) in $H^+$ and $NH_4^+$ forms was studied in the presence of water-miscible alcohols: methanol, ethanol, 1-propanol, and 2-propanol. The effects of these organic solvents observed in the exchange behavior have been explained on the basis of increased ion association in the resin phase. The anomalous behavior of $NH_4^+$ in the presence of organic solvents is also explained.

## Introduction

It has generally been observed that addition of organic solvents to the solution phase enhances the affinities of monovalent cations toward the exchanger.[2–10] A few probable explanations in terms of the dielectric constant of the solution phase,[9,10] ion association,[6,11,12] solvation of ions,[2b–7] etc., have been put forward to account for the phenomenon, based on limited experimental data. There are some experimental results, which are not adequately explained; for example, reversal of affinities of $Li^+$ and $H^+$[9] or $NH_4^+$ and $Na^+$[2b,6] with increase of organic solvent in the solution phase.

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(1) Part of this work has been presented at the 50th session of the Indian Science Congress, Delhi, 1963.

(2) (a) G. Wiegner and H. Jenny, *Kolloid Z.*, **42**, 268 (1927); (b) T. R. E. Kressman and J. A. Kitchener, *J. Chem. Soc.*, 1211 (1949).

(3) T. Sakaki and H. Kakihana, *Kagaku* (Tokyo), **23**, 471 (1953).

(4) B. Sensoni, *Angew. Chem.*, **66**, 330 (1954).

(5) O. D. Bonner and J. C. Moorefield, *J. Phys. Chem.*, **58**, 555 (1954).

(6) R. W. Gable and H. A. Strobel, *ibid.*, **60**, 513 (1956).

(7) H. Okuno, M. Honda, and K. Ishimori, *Japan Analyst*, **2**, 428 (1953).

(8) S. L. Bafna, *J. Sci. Ind. Res.* (India), **12B**, 613 (1953).

(9) T. Sakaki, *Bull. Chem. Soc. Japan*, **28**, 217 (1955).

(10) G. M. Panchenkov, V. I. Gorshkov, and M. V. Kulanova, *Zh. Fiz. Khim.*, **32**, 616 (1958).

(11) C. W. Davies and B. D. R. Owen, *J. Chem. Soc.*, 1676 (1956).

(12) H. P. Gregor, D. Nobel, and M. H. Gottlieb, *J. Phys. Chem.*, **59**, 10 (1955).