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Neutron diffraction study of $Mn(NO_3)_2 \cdot 4H_2O$

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Auszug

Die Intensitäten von 629 unabhängigen Reflexen wurden mit einem Neutronendiffraktometer gemessen und die Lagen der Wasserstoffatome in der Struktur von $Mn(NO_3)_2 \cdot 4H_2O$ bestimmt. Die Kleinste-Quadrate-Verfeinerung mit isotropen Temperaturfaktoren für alle Atome führte zu einem R-Wert von 0,10. Die Wasserstoffbindungen der Struktur sind ungegabelt und schwach; sie variieren zwischen 2,72(2) und 2,88(2) Å. Die (H—O—H)- und (O—H···O)-Winkel liegen zwischen 103(2) und 109(2)° beziehungsweise zwischen 152(2) und 177(2)°.

Abstract

Positions of the hydrogen atoms in the structure of $Mn(NO_3)_2 \cdot 4H_2O$, were determined from 692 independent intensities, measured on a neutron diffractometer at the RA reactor in Vinča. The positional and isotropic thermal parameters for all atoms were refined by least squares to an R value of 0.10. All hydrogen interactions in the structure are normal, not bifurcated, and weak, ranging from 2.72(2) to 2.88(2) Å. The H—O—H and O—H···O angles are between 103(2) and 109(2)°, and 152(2) and 177(2)°, respectively.

Introduction

The crystal structure of $Mn(NO_3)_2 \cdot 4H_2O$ was determined from x-ray photographic data (Popov *et al.*, 1973). Possible hydrogen bonds were assumed on the basis of oxygen-oxygen distances and their angles.

To determine positions of hydrogen atoms and to establish hydrogen network with security neutron-diffraction study of $Mn(NO_3)_2 \cdot 4\,H_2O$ was carried out. For neutrons, the hydrogen atoms in $Mn(NO_3)_2 \cdot 4\,H_2O$ represent 27% of the scattering power, calculated as $\sum\limits_{\substack{\text{H}\\\text{atoms}}} b / \sum\limits_{\substack{\text{all}\\\text{atoms}}} b$.

Experimental

Single crystal of $Mn(NO_3)_2 \cdot 4\,H_2O$, suitable for neutron diffraction were prepared by recrystalization of Merck salt. They are monoclinic, $a = 5.378(10)$, $b = 27.41(10)$, $c = 5.80(3)$ Å, $\beta = 113.5(4)^\circ$, the space group $P2_1/n$ (Popov *et al.*, 1973). The intensities were recorded using a manually operated "MAN" diffractometer with a θ—2θ step scanning technique (at the Boris Kidrič Institute, Vinča). About 20 minutes was spent measuring each reflection. One standard reflection was measured at regular intervals to provide a check on crystal and electronic stabilities. No significant variations were observed. A total of 859 (692 observed) independent reflections were measured from a crystal of cylindrical shape (0.25×0.35 cm). The crystal was enclosed in the spherical quarz wessel to be protected from atmospheric effects. The intensities were corrected for Lorentz and polarization effects but not for absorption and extinction effects. Signs were attached to observed structure factors using x-ray coordinates (Popov *et al.*, 1973) and a three-dimensional Fourier synthesis yielded the positions of hydrogen atoms, which were not determined before. Parameters of all atoms were refined by full-matrix least-squares calculations. The quantity minimized was $w(F_0 - F_c)^2$, w being taken as unity for all reflections. After several cycles of refinement, with isotropical thermal parameters for all atoms, the conventional agreement factor of 0.10 was achieved. The coherent neutron scattering amplitudes employed were: $\text{Mn} = -0.390$; $\text{O} = 0.580$; $\text{N} = 0.940$; $\text{H} = -0.370$, all $\times 10^{-12}$ cm (Bacon, 1972). In the analysis, programs VINČA 1 (local data reduction program), FORDAP, NUCLS and SADIANA (from Ibers's system of crystallographic programs) were used on the CDC-3600 computer.

Results and discussion

Figures 1 and 2 show the crystal structure of $Mn(NO_3)_2 \cdot 4\,H_2O$, including hydrogen atoms, viewed down c and a axes. The list of observed and calculated structure factors is given in Table 1. The obtained atomic position and thermal parameters with their estimated

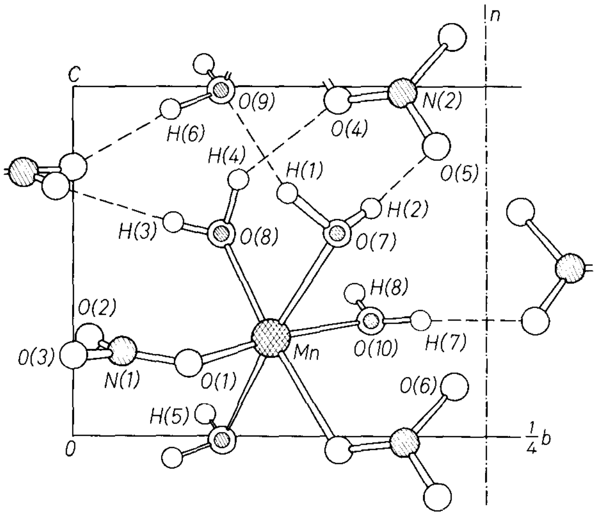

Fig. 1. The crystal structure of $Mn(NO_3)_2 \cdot 4H_2O$ viewed along a axis

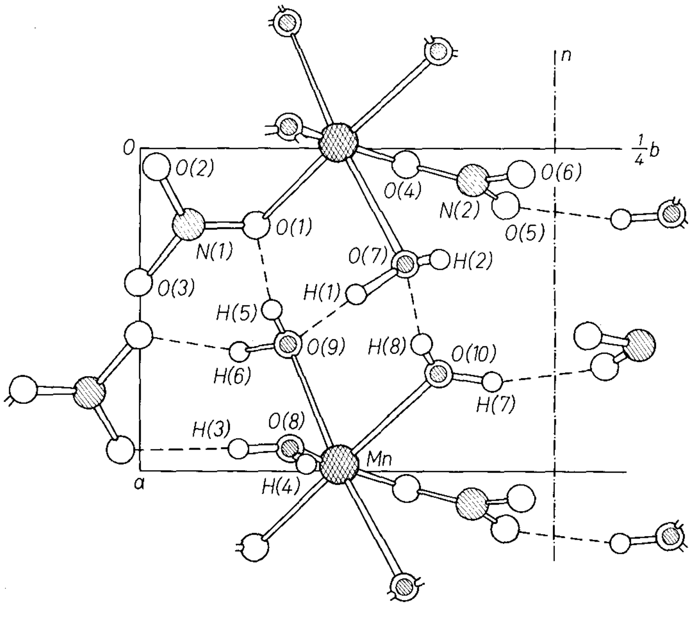

Fig. 2. The crystal structure of $Mn(NO_3)_2 \cdot 4H_2O$ viewed along c axis

Table 1. *List of observed and calculated structure factors*

h	k	l	$\lvert F_o \rvert$	$\lvert F_c \rvert$
0	6	0	5.43	4.69
	8		1.79	1.05
	10		5.25	4.98
	12		6.57	6.75
	14		4.75	4.82
	16		8.16	7.94
	18		1.75	1.52
	20		0.39	0.32
	22		1.13	1.41
	26		2.54	1.99
0	4	1	6.39	5.89
	5		6.95	6.52
	6		5.58	5.20
	7		4.53	4.08
	8		6.16	5.85
	9		3.60	3.43
	10		0.81	0.75
	11		2.10	2.19
	12		4.82	4.56
	14		1.60	2.03
	18		6.10	5.80
	19		1.93	1.98
	20		0.52	0.46
	21		1.46	1.47
	22		1.89	1.85
	23		0.55	0.54
	25		1.02	0.75
	26		2.02	2.05
	27		1.43	1.36
	28		0.98	0.83
	29		1.31	0.91
	30		1.41	0.95
	34		0.44	0.14
0	0	2	0.72	0.30
	2		9.81	9.32
	3		1.59	1.46
	5		1.63	1.55
	6		2.87	2.71
	7		2.53	2.34
	8		1.09	1.01
	9		1.20	1.30
	10		1.21	1.25
	12		2.51	3.11
	14		0.70	0.55
	15		2.52	2.52
	16		2.62	2.93
	18		1.07	0.94
	20		3.55	3.83
	21		0.69	0.67
	22		1.28	1.02
	23		1.23	1.31
	24		3.05	2.80
	25		1.03	1.21
	27		0.81	0.84
	29		0.87	0.70
0	2	3	5.65	5.75
	4		1.07	1.18
	8		1.95	2.46
	9		2.03	1.85
	11		3.95	4.24
	12		3.18	3.32
	13		1.32	1.52
	14		5.39	5.78
	16		3.50	3.67
	17		2.36	2.63
	18		1.35	1.53
	19		1.52	1.58
	24		1.00	0.95
	25		1.00	0.91
	31		0.98	0.67
0	0	4	4.77	4.81
	1		0.88	0.65
	2		2.58	3.08
	4		2.69	3.06
	5		1.86	1.98
	6		2.89	3.11
	7		0.64	0.76
	8		1.63	1.59
	9		0.48	0.54
	10		1.81	2.05
	11		1.22	1.07
	12		0.38	0.41
	13		1.43	1.37
	14		0.68	0.65
	15		0.66	0.65
	16		0.69	0.76
	17		0.66	0.75
	18		0.92	1.01
	19		0.65	0.54
	20		0.99	0.85
	21		0.46	0.39
	22		1.48	1.38
	23		1.82	1.66
	24		0.98	0.76
	29		0.62	0.45
	31		0.37	0.28
0	1	5	3.19	2.89
	2		2.01	1.84
	3		1.86	1.53
	4		2.43	2.28
0	5	5	0.81	1.03
	6		0.97	1.12
	7		1.22	1.13
	8		0.73	0.82
	9		1.31	1.06
	10		2.29	2.18
	12		0.95	0.85
	13		0.89	0.94
	15		0.57	0.53
	16		0.45	0.63
	18		0.30	0.34
	19		0.37	0.39
	21		0.67	0.57
	25		0.84	0.81
	26		1.24	0.70
	27		0.36	0.26
0	0	6	0.72	0.47
	1		0.76	0.70
	3		0.91	0.96
	5		0.37	0.37
	6		1.24	1.16
	7		0.41	0.19
	8		0.98	0.93
	9		0.44	0.41
	15		0.52	0.61
	17		0.48	0.40
	21		0.41	0.27
0	2	7	0.44	0.22
	3		0.84	0.59
	6		0.98	0.73
	7		0.88	0.54
	10		0.72	0.64
	11		0.41	0.19
0	0	8	0.48	0.26
1	1	0	3.31	2.41
	5		6.40	6.04
	6		10.09	9.21
	8		1.41	1.19
	9		1.10	0.84
	10		7.05	7.15
	12		5.02	4.38
	13		3.31	2.96
	14		1.90	1.83
	15		0.73	0.50
	16		3.64	3.54
	17		2.47	2.56
	18		1.51	1.49
	19		1.05	0.69
	20		4.57	4.87
	21		1.90	1.86
	22		0.60	0.24
	24		3.31	3.19
	25		0.22	0.20
	26		0.99	0.68
	27		1.51	1.17
	28		0.77	0.78
	30		0.54	0.53
	31		0.50	0.57
	32		0.64	0.47
	33		0.97	0.82
	36		0.61	0.18
1	1	1	2.38	2.27
	2		10.96	10.42
	3		2.69	2.56
	4		2.08	1.84
	5		5.67	5.34
	6		1.02	0.83
	7		1.43	1.80
	9		1.39	1.59
	10		4.25	4.10
	11		1.01	0.92
	12		2.96	3.02
	13		0.72	0.69
	14		1.77	2.02
	16		0.77	0.61
	17		0.47	0.56
	18		4.84	4.71
	20		3.28	3.08
	21		1.63	1.37
	22		1.47	1.25
	23		0.80	0.81
	24		0.54	0.16
	25		1.19	0.87
	26		0.44	0.38
	30		0.72	0.48
	31		1.26	0.90
	34		0.44	0.29
	36		0.58	0.50
1	1	2	1.64	1.50
	3		3.90	4.13
	4		4.86	5.29
	5		1.54	1.64
	6		3.17	3.39
	7		2.73	2.89
	8		2.01	2.36
	9		2.55	2.50
	10		2.67	2.88
	11		0.99	0.86
	14		2.54	2.49
	15		1.59	1.77
1	16	2	1.60	1.97
	17		0.58	0.72
	18		0.46	0.33
	19		2.66	2.74
	20		2.13	1.96
	21		1.19	1.12
	22		0.37	0.07
	23		0.88	1.21
	26		0.88	0.86
	27		0.78	0.95
	29		0.48	0.68
	30		0.50	0.54
1	1	3	1.02	1.12
	2		2.47	3.16
	3		1.25	1.24
	4		2.38	2.26
	6		5.13	5.54
	7		0.42	0.49
	9		1.91	1.94
	10		0.52	0.22
	12		0.74	0.70
	13		3.25	3.49
	14		2.44	2.42
	15		0.71	0.82
	16		0.52	0.31
	17		0.28	0.32
	18		0.73	0.76
	19		0.93	0.74
	20		1.41	1.22
	21		1.53	1.52
	22		3.32	3.32
	23		1.19	1.06
	24		0.81	0.57
	25		0.76	0.48
	27		0.58	0.61
	28		0.23	0.30
	29		0.40	0.37
	30		0.51	0.56
1	4	4	2.12	2.40
	5		1.67	1.75
	10		0.59	0.64
	11		0.52	0.57
	12		2.99	2.98
	13		0.89	0.80
	16		1.72	1.58
	17		0.75	0.53
	21		1.10	0.94
	23		1.05	1.04
1	2	5	2.75	2.79
	4		1.23	1.41
	8		1.24	1.22
	12		0.94	0.98
1	5	6	0.93	0.85
	8		1.49	1.20
2	0	0	4.13	4.19
	1		6.39	6.52
	2		3.35	3.29
	3		3.25	3.24
	4		3.86	3.41
	5		2.43	2.35
	6		2.81	2.62
	7		0.43	0.14
	8		1.50	1.35
	9		1.93	1.88
	10		3.03	2.67
	11		4.72	4.48
	12		2.77	2.75
	13		0.78	0.71
	14		2.93	2.89
	15		0.59	0.60
	16		0.44	0.22
	18		2.59	2.35
	19		0.59	0.55
	20		4.63	4.37
	21		1.23	1.25
	23		0.39	0.35
	24		1.59	1.36
	25		1.21	1.14
	26		0.57	0.34
	28		1.14	0.76
	29		0.56	0.37
	31		0.57	0.27
	32		0.65	0.65
	33		0.62	0.56
	35		0.46	0.30
	36		0.55	0.24
2	2	1	2.59	2.42
	3		2.90	3.05
	4		6.03	6.28
	5		3.06	3.13
	7		1.75	1.75
	8		6.45	6.56
	12		2.55	2.65
	14		3.72	3.62
	18		5.12	5.21
	19		2.70	2.70
	22		1.89	1.74
	24		1.03	0.96
	26		2.86	2.59
	28		0.97	0.80
2	1	2	1.00	1.15
	3		2.88	3.23
	4		2.98	2.88
	6		0.65	0.75
	7		0.99	1.07
	8		0.35	0.34
	9		2.90	3.02
	11		1.58	1.65
	12		0.66	0.66
	14		0.50	0.42
	17		0.64	0.78
	18		1.71	1.81
	19		1.40	1.20
	20		1.51	1.34
	21		0.55	0.57
	22		1.85	1.76
	24		0.57	0.44
	25		0.86	0.97
2	1	4	0.37	0.22
	2		1.47	1.57
	3		1.13	1.57
	4		0.82	0.89
	6		0.67	0.78
	8		0.71	0.66
	9		0.46	0.66
	11		1.13	1.04
	12		0.96	0.86
	14		1.40	1.04
	15		1.78	1.63
	16		0.70	0.56
	17		0.75	0.63
	18		0.54	0.34
	19		1.17	1.01
	20		2.02	1.51
	21		0.91	0.77
	22		0.31	0.27
	23		0.72	0.80
	25		0.57	0.30
2	10	5	0.87	0.74
	14		0.92	0.64
2	0	6	1.37	1.07
	6		0.40	0.32
3	1	0	0.77	0.69
	2		0.86	0.67
	5		1.76	1.71
	6		1.26	1.31
	7		2.95	2.93
	9		2.32	2.70
	10		0.56	0.26
	11		2.72	2.60
	12		1.26	1.36
	13		3.02	2.97
	14		1.76	1.48
	15		1.71	1.27
	16		2.66	1.76
	17		1.35	1.18
	18		0.49	0.27
	20		3.19	3.14
	21		1.18	1.12
	22		2.57	2.27
	23		0.31	0.16
	24		0.62	0.58
	25		1.18	0.71
	26		2.27	1.71
	27		0.23	0.01
	28		0.64	0.50
	29		0.74	0.67
	30		1.73	0.82
	32		0.60	0.45
3	0	1	0.78	0.89
	2		2.02	2.29
	3		2.97	3.57
	4		1.23	1.49
	6		2.41	2.32
	8		2.88	3.01
	9		2.56	2.65
	10		1.28	1.66
	12		0.77	0.74
	14		1.81	1.75
	16		2.48	2.13
	18		2.71	2.22
	20		1.23	0.93
	22		2.20	1.97
	26		0.30	0.23
3	1	2	2.08	2.51
	2		2.01	2.25
	4		0.87	1.13
	5		2.15	2.18
	6		2.20	2.70
	9		0.68	0.71
	11		1.62	1.55
	17		1.20	1.14
	18		2.03	1.98
	20		0.98	1.16
	21		0.93	0.76
	22		1.09	0.96
	24		2.46	2.00
	26		0.50	0.46
	28		1.26	0.84
	30		0.66	0.39
3	0	3	0.61	0.86
	1		0.77	0.94
	5		0.63	0.70
	6		1.33	1.51
	7		1.26	1.34
	9		0.57	0.54
	11		1.04	1.01
	12		1.19	1.08
	13		1.08	1.14
	14		1.34	1.19
	15		0.55	0.58
	16		0.79	0.60
	17		1.17	0.87
	18		1.43	1.31
	19		0.46	0.45
	20		1.08	0.87
	22		0.94	0.55
	23		0.96	0.83
	27		0.44	0.43
4	0	0	1.30	1.29
	2		2.65	2.80
	3		0.39	0.27
	4		1.81	1.74
	6		1.52	1.66
	7		0.70	0.39
	8		1.49	1.37
	9		1.45	1.24
	10		2.78	2.68
	11		0.30	0.11
	12		0.56	0.65
	13		1.67	1.68
	14		1.70	1.97
	15		0.84	0.87
	16		1.18	0.82
	19		0.34	0.13
	20		2.68	1.97
	21		2.07	1.77
	23		0.67	0.52
	24		1.85	1.42
	25		0.48	0.39
	27		1.15	0.74
	28		1.01	0.70
	29		0.74	0.45
4	2	1	2.30	2.36
	6		1.53	1.63
	7		2.80	3.09
	9		2.50	2.89
	14		1.97	1.79
	22		0.51	0.42
4	0	2	2.39	2.39
	3		0.65	0.67
	4		0.70	0.99
	8		1.29	1.25
	20		0.52	0.51
4	3	4	0.52	0.44
	4		0.29	0.20
	5		0.27	0.29
	9		0.60	0.47
	10		0.65	0.59
	11		0.56	0.45
5	1	0	0.57	0.44
	3		1.74	1.64
	4		1.35	1.00
	5		0.77	0.60
	6		1.37	1.25
	10		0.96	0.86
	11		0.42	0.19
	12		0.83	1.01
	13		1.25	1.05
	15		0.56	0.56
	16		0.62	0.35
	17		0.54	0.35
	18		1.03	0.90
5	3	1	0.50	0.83
	4		1.80	1.78
6	0	0	2.02	2.00
	1		0.66	0.49
	3		0.51	0.33
	4		0.78	0.56
	5		0.78	0.54
	7		0.97	0.65
	9		1.43	1.10
	10		0.99	0.88
	11		0.69	0.36
	13		0.43	0.36
	15		0.34	0.11
	18		1.05	0.49
-1	0	1	12.10	11.75
	1		4.79	4.09
	2		2.34	2.02
	3		2.38	1.82
	4		5.52	5.17
	6		2.16	1.97
	8		0.67	0.66
	9		2.45	2.57
	10		1.43	1.44
	11		1.86	2.03
	12		2.55	2.65
	14		3.03	3.12
	21		2.37	2.53

Table 1. *(Continued)*

h	k	l	$\|F_o\|$	$\|F_c\|$
-1	22	1	4.55	4.74
	23		1.26	1.36
	26		1.26	0.79
	27		0.97	1.12
	30		1.57	1.36
-1	2	2	0.78	0.83
	3		2.26	2.14
	4		8.73	8.41
	5		0.68	0.66
	8		4.87	4.92
	9		2.65	2.51
	10		3.24	3.89
	14		4.71	4.92
	20		4.61	4.76
	26		1.22	1.15
	29		1.32	0.82
	30		1.15	0.90
-1	0	3	3.16	3.54
	1		3.63	3.31
	2		3.89	4.41
	6		2.14	2.26
	9		1.48	1.43
	11		3.20	3.49
	16		0.95	1.21
	18		0.53	0.65
	23		1.34	1.16
	24		1.78	1.64
	25		1.41	1.22
	31		0.63	0.72
	32		1.03	0.87
-1	2	4	2.72	2.84
	3		1.38	1.46
	4		2.90	2.93
	6		1.81	2.02
	7		1.53	1.62
	8		4.20	4.84
	11		2.65	2.85
	19		2.75	2.74
	20		0.93	1.04
-1	21	4	0.65	0.56
	22		0.84	0.76
	24		2.17	1.67
	28		1.69	1.26
-1	0	5	1.12	1.08
	1		2.34	2.67
	7		1.59	1.74
	8		0.42	0.28
	12		0.99	1.14
	14		1.04	1.47
	16		0.93	0.83
-1	4	6	1.66	1.59
	5		1.07	0.93
	6		1.06	1.20
	8		2.24	1.83
	12		1.01	0.93
-2	2	1	8.21	8.52
	3		2.25	2.55
	6		1.55	2.11
	9		2.63	2.81
	10		3.20	3.14
	14		3.88	4.30
	15		1.87	2.11
	16		2.53	2.91
	18		2.57	2.74
	22		3.55	3.81
	24		3.26	3.32
	30		1.06	1.11
	32		1.27	1.11
-2	0	2	6.48	6.31
	2		0.22	0.17
	6		2.23	2.19
	8		2.42	2.68
	9		3.39	3.32
	10		3.22	3.75
	14		3.06	3.66
	15		2.60	3.00
	18		0.94	1.10
	19		3.28	3.40
-2	20	2	3.99	3.87
	21		3.16	3.42
	22		1.43	1.49
	23		2.74	2.80
	31		0.68	0.61
-2	1	3	2.02	2.08
	2		4.44	4.69
	4		2.28	2.58
	8		1.83	2.10
	12		2.95	3.70
	13		3.68	4.23
	16		2.30	2.50
	17		2.10	2.31
	18		2.35	2.12
	19		1.39	1.76
	20		0.81	0.58
	22		1.26	1.20
	24		1.93	2.02
	25		0.69	0.68
	26		2.98	2.94
	30		1.40	1.23
	31		0.66	0.49
-2	0	4	1.85	2.01
	9		1.56	1.64
	10		0.43	0.53
	12		1.51	1.88
	16		2.55	2.96
	17		1.15	1.16
	18		2.41	3.26
	19		1.25	1.35
	20		0.91	1.12
	21		0.31	0.59
	22		1.31	1.27
-2	3	5	1.43	1.56
	5		1.92	1.62
	6		3.21	3.08
	7		1.04	1.26
	8		2.41	2.27
	10		1.68	1.81
-2	18	5	1.65	1.80
	22		1.33	1.28
	24		0.97	0.86
-2	0	6	1.07	1.12
	1		3.19	3.25
	9		1.04	1.17
	12		1.13	1.08
	13		0.78	0.70
	14		1.01	0.94
	15		2.00	1.88
	18		1.00	0.88
-3	3	2	1.02	1.13
	6		4.16	4.42
	9		2.78	2.77
	11		2.78	3.00
	15		2.68	2.75
	22		0.76	1.02
	24		2.46	2.37
	28		2.20	1.94
-3	0	3	1.39	1.45
	3		0.22	0.25
	5		1.72	1.83
	6		2.74	3.10
	7		3.77	4.37
	8		0.98	0.99
	14		2.14	2.44
	16		3.94	4.07
	20		3.06	3.24
	23		1.22	1.02
	24		0.85	1.01
-3	4	4	2.81	3.25
	8		2.15	2.46
	14		2.13	2.28
	19		1.64	1.59
	20		2.05	1.93
	26		1.29	1.32
-3	0	5	1.92	1.90
	2		1.76	1.76
	3		2.72	2.76
-3	4	5	2.41	2.50
	5		2.86	3.04
	7		2.21	2.00
	8		1.11	1.37
	12		1.64	1.61
	16		1.12	0.89
	17		1.51	1.37
-4	4	1	2.55	2.80
	7		0.90	0.68
	8		2.62	2.65
	15		0.51	0.57
	16		1.02	0.77
-4	0	2	2.82	3.11
	1		2.41	2.58
	2		2.87	3.14
	5		1.33	1.56
	8		1.65	2.13
	18		3.47	3.58
	24		0.54	0.95
-4	0	4	1.74	1.74
	1		2.40	2.79
	4		2.09	2.30
-5	2	1	3.24	3.23
	11		1.61	1.62
	12		2.04	1.83
	17		0.58	0.65
-5	2	2	1.92	1.81
	6		1.22	1.36
	8		1.98	2.18
	16		0.92	1.05
-5	0	5	2.25	2.15
	1		1.43	1.25
	5		0.47	0.28
-6	0	4	1.18	1.30
	1		0.91	1.13
-8	0	4	0.40	0.25

standard deviations are given in Table 2. Below the values for positional coordinates of nonhydrogen atoms determined in this study are the corresponding values established in the x-ray crystal-structure analysis (Popov *et al.*, 1973). Since these data are in good agreement the structure features of manganese octahedra and nitrate groups will not be discussed here.

Detailed geometry of water molecules and hydrogen bonds is given in Table 3.

The crystal structure of $Mn(NO_3)_2 \cdot 4H_2O$ is built up of the layers of manganese octahedra, separated by two layers of nitrate ions. Hydrogen bonds join the octahedra and nitrate groups in the layer, as well as the layers themselves. The acceptor atoms for hydrogen bonds are nitrate oxygen and water oxygen atoms. All hydrogen bond interactions in the structure are weak, the range of O—H···O distances being 2.72(2) to 2.88(2) Å. These values are within the range of values reported for other hydrogen bonds found in the crystalline hydrates studied by neutron difraction (Hamilton and Ibers, 1968; Ferraris and Franchini-Angela, 1972). Almost all H—O distances are shorter than expected but, except for O(7)—H(2), still in the range of the values reported in the literature. The distance O(7)—H(2) is for six standard deviations shorter than the mean value of H—O distances determined by neutron diffraction, 0.96 Å (Ferraris and

Table 2. *The final atomic parameters with significant figures of estimated standard deviations in parentheses*

Atom	x	y	z	B
Mn	0.977(2) 0.980(1)	0.1244(4) 0.1256(1)	0.278(2) 0.281(1)	5.0(2) Å^2
O(1)	0.250(2) 0.244(3)	0.0719(3) 0.0737(5)	0.201(2) 0.203(2)	6.0(2)
O(2)	0.055(2) 0.056(2)	0.0112(3) 0.0090(4)	0.277(2) 0.282(2)	5.7(2)
O(3)	0.423(2) 0.426(2)	0.0036(3) 0.0020(4)	0.226(2) 0.223(2)	5.9(2)
O(4)	0.046(2) 0.055(3)	0.1596(3) 0.1591(4)	0.973(2) 0.975(2)	5.9(2)
O(5)	0.184(2) 0.184(3)	0.2215(3) 0.2223(4)	0.830(2) 0.823(2)	6.4(2)
O(6)	0.077(2) 0.087(3)	0.2298(3) 0.2310(5)	0.139(2) 0.141(3)	6.8(2)
O(7)	0.357(3) 0.360(3)	0.1551(3) 0.1550(4)	0.580(2) 0.567(2)	5.6(2)
O(8)	0.930(2) 0.933(2)	0.0876(4) 0.0879(5)	0.585(2) 0.582(3)	7.0(2)
O(9)	0.612(2) 0.624(2)	0.0892(3) 0.0904(4)	−0.008(2) −0.002(2)	5.6(2)
O(10)	0.705(2) 0.710(3)	0.1786(4) 0.1778(5)	0.326(2) 0.327(3)	6.0(2)
N(1)	0.239(1) 0.242(3)	0.0274(2) 0.0281(5)	0.238(1) 0.237(2)	5.1(1)
N(2)	0.102(1) 0.106(3)	0.2054(2) 0.2048(5)	0.981(1) 0.985(3)	5.2(1)
H(1)	0.463(4)	0.1325(7)	0.701(4)	8.2(4)
H(2)	0.339(3)	0.1787(6)	0.646(3)	6.8(3)
H(3)	0.927(4)	0.0557(7)	0.613(3)	7.3(3)
H(4)	0.982(5)	0.1020(8)	0.730(4)	8.6(4)
H(5)	0.496(4)	0.0847(6)	0.056(3)	6.9(3)
H(6)	0.632(4)	0.0606(7)	0.943(4)	7.6(4)
H(7)	0.719(4)	0.2098(6)	0.331(3)	7.2(3)
H(8)	0.611(5)	0.1692(8)	0.414(4)	9.5(5)

Table 3. *The detailed geometry of water molecules and hydrogen bonds in the crystal structure of* $Mn(NO_3)_2 \cdot 4H_2O$

Hydrogen bond	H₂O parameters			Hydrogen bond parameters			
Distances	Distances		Angles	Distances		Angles	
O—H···O	O—H	H—H	H—O—H	O—H···O	H···O	O—H···O	O···O···O
O(7) H(1)···O(9)	0.92(3) Å	1.39(2) Å	109(2)°	2.88(1) Å	1.97(2) Å	168(2)°	97(1)°
H(2)···O(5)	0.78(3)			2.72(2)	1.98(2)	156(2)	
O(8) H(3)···O(2)^{1}	0.89(3)	1.41(3)	107(2)	2.82(1)	1.93(2)	172(2)	104(2)
H(4)···O(4)^{2}	0.87(3)			2.88(2)	2.06(2)	156(2)	
O(9) H(5)···O(1)^{3}	0.85(3)	1.34(3)	103(2)	2.72(2)	1.87(3)	177(2)	97(1)
H(6)···O(3)^{4}	0.86(3)			2.82(1)	1.98(2)	165(2)	
O(10) H(7)···O(5)^{4}	0.86(2)	1.43(3)	109(2)	2.74(1)	1.89(2)	163(1)	107(3)
H(8)···O(7)	0.89(4)			2.88(2)	2.00(3)	171(2)	

The superscripts refer to the following transformation of the atomic coordinates x, y, z:

^{1} $-x$ $1-y$ $-z$

^{2} $1+x$ y z

^{3} x y $1+z$

^{4} $\frac{1}{2}-x$ $\frac{1}{2}+y$ $\frac{1}{2}-z$

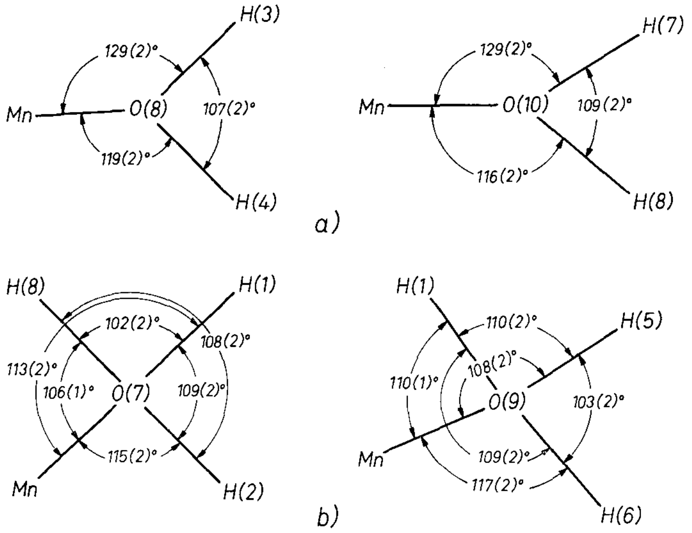

Fig. 3. The geometry of water-oxygen atoms: a) trigonally coordinated O(8) and O(10); b) tetrahedrally coordinated O(7) and O(9)

Franchini-Angela, 1972), indicating that the standard deviation may be underestimated.

Water-oxygen atoms O(8) and O(10) are trigonally coordinated (Fig. 3a). The direction O(8)—Mn is bent out of the plane of H(3)—O(8)—H(4) water molecule by 19(2)°. The directions H(3)—O(2) and H(4)—O(4) make the angles of 1(2) and —5(2)° with respect to the plane of the water molecule. The directions O(10)—Mn, H(7)—O(5) and H(8)—O(7) are bent out of the plane of H(7)—O(10)—H(8) water molecule by 21(2), 5(2) and —7(2)°, respectively. On the basis of modified (Ferraris and Franchini-Angela, 1972) classification proposed by Chidambaram, Sequeira and Sikka (1964), coordination of these two water molecules belongs to Classe 1, type D.

Water-oxygen atoms O(7) and O(9) are in tetrahedral coordination (Fig. 3b). Along the two lone pair orbitals of the atom O(6) there are two cations, Mn and H(8). The plane containing Mn, O(7) and H(8) atoms is nearly perpendicular to the water-molecule plane, making an angle of 92(1)°. The directions O(7)—Mn and O(7)—H(8) make the angles of 43(2) and 62(2)° with respect to the H(1)—O(7)—H(2) water-molecule plane. The directions H(1)—O(9) and H(2)—O(5) are bent out of the plane of the water molecule by —7(2) and —22(2)°.

Along the lone pair orbitals of the water oxygen atom O(9) are also coordinated two cations, Mn and H(1). The planes containing these three atoms make an angle of 87(1)° with the plane of water molecule. The directions O(9)—Mn and O(9)—H(1) make angles of 68(1) and 42(1)° with respect to the water-molecule plane. The directions H(5)—O(1) and H(6)—O(3) are out of this plane by 19(2) and 21(2)°, respectively. The coordination of the water molecules H(1)—O(7)—H(2) and H(5)—O(9)—H(6) is thus Classe 2, type H according to the classification scheme of FERRARIS and FRANCHINI-ANGELA.

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