Neutron Diffraction Study of β-$RbMnCl_3,2H_2O$

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The crystal structure of β-$RbMnCl_3,2H_2O$ has previously been determined by X-ray diffraction.[1] The unit cell dimensions are $a=6.65$ Å, $b=7.01$ Å, $c=9.03$ Å, $\alpha=92.3°$, $\beta=109.4°$ and $\gamma=112.9°$. The space group is $P\bar{1}$. In a paper concerning the structure of $KMnCl_3,2H_2O$ [2] it was pointed out, that these two compounds were isostructural, but it was suggested, that the hydrogen bonding scheme was not identical in the two compounds. The neutron diffraction study was undertaken to clarify this problem. A similar investigation of the potassium compound is in progress.

Single crystals of reasonable size were formed, when a saturated solution of $MnCl_2,4H_2O$ and RbCl (molar ratio 5:1) in 8 M HCl was allowed to stand for several years. All the crystals were twinned with $[01\bar{1}]$ as twin axis. A needle shaped twin was used for data collection; the crystal was oriented along $[01\bar{1}]$, the needle axis. The crystal has the dimensions 4 mm × 0.5 mm × 0.5 mm, and the ratio between the sizes of the twins was approximately 6:1. With this orientation overlapping reflexions occurred only in equator; the intensities of these reflexions therefore were multiplied by 6/7.

The neutron diffraction data were collected on an automatic Hilger-Ferranti four-circle diffractometer located at the Atomic Energy Commission Research Establishment, Risø. The wavelength of the monochromatic neutron beam was 1.025 Å, and the neutron flux at the crystal was 10^6 n/cm²/sec. The reflections were recorded in the A-setting position with the ω-scan technique. A standard reflection, $20\bar{3}$, was measured at intervals of 10. The diffractometer data were reduced to structure factors using an ALGOL program DRAM.[3] 236 observed independent reflexions were obtained; a reflexion was defined to be unobserved, when the intensity was less than three times its standard deviation. No correction for absorption was applied, $\mu=1.31$ cm^{-1}.

Table 1. Positional parameters, isotropic H-temperature factors, B, and anisotropic non-H-temperature factors × 10^{-4} in the form: $\exp(-b_{11}h^2-b_{22}k^2-b_{33}l^2-b_{12}hk-b_{13}hl-b_{23}kl)$. Numbers in brackets are e.s.d. in unit of the last digit.

Atom	x/a	y/b	z/c	B Å²
H_I	0.581 (4)	0.685 (3)	0.461 (3)	4.8 (4)
H_{II}	0.778 (4)	0.817 (3)	0.414 (3)	4.0 (4)
H_{III}	0.640 (4)	0.459 (3)	0.190 (2)	4.4 (4)
H_{IV}	0.735 (3)	0.464 (3)	0.069 (2)	3.4 (4)
O_I	0.743 (2)	0.749 (1)	0.491 (1)	
O_{II}	0.746 (2)	0.438 (1)	0.168 (1)	
Cl_I	0.242 (1)	0.713 (1)	0.495 (1)	
Cl_{II}	0.771 (1)	0.959 (1)	0.187 (1)	
Cl_{III}	0.244 (1)	0.426 (1)	0.162 (1)	
Mn	0.998 (3)	0.331 (2)	0.329 (2)	
Rb	0.256 (2)	0.934 (1)	0.177 (1)	

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
O_I	339 (50)	165 (32)	66 (23)	302 (69)	140 (56)	89 (44)
O_{II}	221 (42)	182 (29)	67 (21)	251 (56)	90 (53)	59 (39)
Cl_I	119 (24)	147 (17)	72 (11)	148 (31)	71 (28)	35 (22)
Cl_{II}	188 (25)	122 (15)	88 (12)	81 (29)	113 (30)	10 (20)
Cl_{III}	209 (27)	137 (18)	116 (14)	124 (36)	217 (36)	99 (26)
Mn	93 (52)	117 (40)	26 (25)	49 (69)	21 (66)	81 (47)
Rb	145 (37)	159 (28)	46 (20)	142 (50)	90 (49)	73 (37)

Table 2. Observed and calculated structure factors.

h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc	h	k	l	Fo	Fc
0	0	3	473	-496	1	-3	-3	154	-144	1	5	-3	135	120	2	1	-7	109	113	4	-5	1	126	141
0	0	4	94	78	1	-3	-1	84	-98	2	-6	-1	72	-85	2	1	-4	86	-85	4	-5	2	76	-78
0	0	6	370	376	1	-3	0	107	123	2	-6	0	213	218	2	1	-1	113	-116	4	-4	-5	320	-315
0	0	8	174	-184	1	-3	1	103	96	2	-6	1	159	162	2	1	5	150	-162	4	-4	-4	149	-144
0	1	-7	70	69	1	-3	2	103	103	2	-6	2	100	112	2	2	-5	514	-529	4	-4	-3	133	-140
0	1	-5	70	65	1	-3	3	101	-108	2	-6	3	302	-315	2	2	-4	96	102	4	-4	-2	295	292
0	1	-3	70	65	1	-2	-7	113	-119	2	-6	4	144	-125	2	2	-2	435	439	4	-4	-1	140	129
0	1	-2	76	-65	1	-2	-4	112	127	2	-5	-2	96	107	2	2	-1	98	-105	4	-4	0	119	105
0	1	0	101	85	1	-2	-2	120	112	2	-5	-1	214	-205	2	2	1	375	-364	4	-4	1	467	-446
0	1	1	65	64	1	-2	-1	78	-85	2	-5	2	83	78	2	2	2	148	166	4	-4	4	354	327
0	1	2	80	-74	1	-2	2	128	-120	2	-5	4	110	95	2	2	3	117	126	4	-3	-6	71	66
0	1	4	92	98	1	-1	-3	72	79	2	-4	-5	229	227	2	2	4	212	219	4	-3	-2	75	75
0	1	5	66	69	1	-1	-2	251	-270	2	-4	-4	178	205	2	3	-1	75	66	4	-3	2	115	106
0	2	-5	409	401	1	-1	0	85	-74	2	-4	-3	128	114	2	3	0	198	-215	4	-2	-7	338	352
0	2	-2	464	-493	1	-1	1	174	191	2	-4	-2	343	-318	2	3	1	76	73	4	-2	-6	118	116
0	2	0	103	91	1	-1	2	64	54	2	-4	-1	114	-134	2	3	3	113	113	4	-2	-5	148	168
0	2	1	317	305	1	-1	3	67	59	2	-4	1	387	374	2	4	-4	367	-395	4	-2	-4	498	-503
0	2	2	76	-70	1	-1	4	114	-105	2	-4	2	101	105	2	4	-3	145	145	4	-2	-1	403	398
0	2	3	97	-89	1	-1	6	73	67	2	-4	3	72	87	2	4	-2	98	96	4	-2	2	454	-464
0	2	4	392	-398	1	0	-2	66	54	2	-4	4	434	-451	2	4	-1	282	258	4	-1	1	80	-92
0	2	5	136	140	1	0	-1	89	77	2	-3	-6	164	-145	2	4	0	121	-122	4	0	-6	430	450
0	3	-6	130	-114	1	0	0	45	35	2	-3	-4	59	-56	3	-6	-1	73	74	4	0	-4	79	81
0	3	-3	91	-103	1	0	3	200	-205	2	-3	-3	77	70	3	-6	3	86	86	4	0	-3	545	-543
0	3	0	133	133	1	1	-7	141	-115	2	-3	-1	83	80	3	-5	-1	75	-76	4	0	0	342	341
0	3	3	178	-161	1	1	-4	61	53	2	-3	0	227	-224	3	-4	-5	186	-210	4	1	-4	88	-107
0	3	5	99	87	1	1	-1	252	-264	2	-3	1	69	81	3	-4	-2	71	70	4	1	-3	72	76
0	4	-6	102	86	1	1	2	138	131	2	-3	2	88	-87	3	-4	2	83	81	4	1	-1	118	118
0	4	-5	144	129	1	2	-7	99	99	2	-3	5	71	76	3	-3	-1	79	84	4	2	-5	369	388
0	4	-4	322	336	1	2	-5	68	68	2	-2	-7	376	-386	3	-3	0	128	-128	4	2	-2	402	-402
0	4	-3	68	-66	1	2	-3	59	62	2	-2	-6	100	-91	3	-2	-4	166	-158	4	2	-1	102	87
0	4	-1	407	-399	1	2	-2	104	-103	2	-2	-5	79	-83	3	-2	3	69	89	4	3	-3	152	-151
0	4	0	108	113	1	2	-1	120	116	2	-2	-4	408	394	3	-1	-5	72	-57	4	3	-2	76	91
0	4	1	123	105	1	2	0	60	72	2	-2	-3	157	168	3	-1	0	67	65	5	-4	-5	106	126
0	4	2	214	206	1	2	1	100	88	2	-2	-1	451	-457	3	-1	1	123	-145	5	-4	-3	104	105
0	5	-2	130	-145	1	2	2	77	-84	2	-2	2	434	458	3	0	-6	71	-66	5	-4	-2	135	-146
0	5	-1	75	73	1	2	4	188	-194	2	-2	5	472	-475	3	0	0	111	-106	5	-3	-3	121	-134
0	5	1	147	155	1	2	5	75	66	2	-2	6	70	69	3	0	3	76	79	5	-2	-4	101	93
0	6	-4	152	155	1	3	-6	155	-136	2	-1	-7	73	76	3	1	-4	60	-59	5	-2	-1	83	-97
1	-6	2	123	114	1	3	-4	63	65	2	-1	-5	145	-140	3	1	-2	90	86	5	-2	0	73	71
1	-5	0	107	124	1	3	-1	100	-109	2	-1	1	147	-131	3	1	2	114	-129	5	-1	-2	125	-155
1	-5	1	87	76	1	3	0	129	-145	2	0	-6	514	-519	3	2	-5	170	-149	5	-1	2	83	-77
1	-4	-5	136	141	1	3	2	89	81	2	0	-3	491	492	3	2	1	100	-138	5	0	-1	79	76
1	-4	-3	115	125	1	4	-6	150	137	2	0	0	459	-486	3	3	-1	100	95	5	1	-1	116	-126
1	-4	-2	154	-159	1	4	-4	140	121	2	0	1	116	116	3	4	-4	161	-163	5	2	-2	92	-88
1	-4	3	78	84	1	4	-3	99	-92	2	0	2	92	99	4	-5	-4	113	-117	6	-2	-1	313	-315
1	-4	4	125	-128	1	4	-1	144	-129	2	0	3	391	393	4	-5	-2	96	-89	6	-1	-2	142	-133
1	-4	5	77	75	1	4	0	131	129	2	0	4	90	-113	4	-5	-1	88	98	6	0	-3	286	285
1	-3	-4	73	72	1	4	2	78	71															

Table 3. Geometry of the hydrogen bonds. O—Cl distances are from X-ray data. Standard deviations of the distances are 0.02 Å (X-ray data) and 0.03 Å (neutron data). Standard deviations of the angles are 2°.

Hydrogen bonds	Distances (Å)			Angles (degrees)	
	O—Cl	H—Cl	O—H	O—H—Cl	H—O—H
O_I (Cl_I, H_I, Cl_{III})	3.29	2.46	0.92	145	
	3.47	2.84		127	109
O_I (H_{II}—Cl_{II})	3.19	2.31	0.90	166	
O_{II} (H_{III}—Cl_{III})	3.29	2.47	0.85	159	
O_{II} (H_{IV}—Cl_{III})	3.18	2.28	0.91	172	109

Structure factors were calculated using the coordinates and isotropic temperature factors of the non-hydrogen atoms from the X-ray work. Nuclear scattering lengths, $b_{Rb}=0.58$, $b_{Mn}=-0.36$, $b_{Cl}=0.96$, $b_O=0.588$ $b_H=-0.372$ (10^{-12} cm). A three dimensional Fourier synthesis was evaluated using signs from these calculations. In the Fourier maps all H-atoms appeared clearly. With the ALGOL-program D445,[4] the parameters of the H-atoms and isotropic temperature factors of all atoms were refined to a conventional R-value of 8.0 %. The refinement was continued with the block-diagonal least-squares program, G403;[5] with this program all atom coordinates, isotropic hydrogen temperature factors and anisotropic nonhydrogen temperature factors (80 parameters including scale factor) were refined to an R-value of 5.6 %. Table 1 gives the coordinates and temperature factors and Table 2 the observed and calculated structure factors. The coordinates are in agreement with the corresponding X-ray coordinates within standard deviation.

The geometry of the hydrogen bonds appears from Table 3. This bonding scheme is in accordance with the proposal in the X-ray work with the exception, that the existence of the bifurcated hydrogen bond from H_I was not foreseen. The O—H distances seem to be rather short, especially the $O_{II}—H_{III}$ distance (0.85 Å). The deviation from the normal value 0.97 Å in water molecules is probably not significant. The absence of correction for thermal motion is most likely the reason for the difference. In $FeSiF_6,6H_2O$ (Hamilton [6]) the calculated correction to be added to the smallest O—H distance is 0.07 Å using the "riding motion" method.

The lone pair coordination of the water molecules is of the type D (Chidambaram *et al.*[7]), in which the bisector of the lone pairs of the oxygen atom points towards the bivalent ion Mn^{2+}; the groups $Mn—OH_2$ are planar.

Recently El Saffar [8] has calculated the coordinates of the hydrogen atoms in β-$RbMnCl_3,2H_2O$ using Baur's least electrostatic energy method.[9] His results are in good agreement with the corresponding coordinates from this neutron study.

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Nitriles from Vilsmeier-Haack Formylations of Primary Nitro Compounds

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In connection with work on 5-nitro-4*H*-cyclopenta[b]thiophene,[1] the thiophene derivative I was a key intermediate, available from 2,3-dibromothiophene in six steps.[1] In search for an easier route to I, Vilsmeier formylation of β-(3-thienyl)-nitroethane (II) was considered worth trying. Formylations according to Vilsmeier-Haack have found extensive use in the thiophene series.[2—4] Thus, 3-methylthiophene (which is closely related to II) has been formylated in 62 % yield to give a mixture of 2- and 5-formyl-3-methylthiophene in the relative proportion 85:15.[5] Although substrates with nitro groups at aromatic positions have been reported to undergo normal Vilsmeier-Haack formylations,[6,7] reports on the application of this method to compounds with aliphatic nitro groups have, to the author's knowledge, not appeared.

Compound II was prepared by reduction of β-(3-thienyl)nitroethylene [8] with sodium borohydride in 70 % yield. The formylating reagent was prepared at 10—20°C from phosphorus oxychloride and *N*,*N*-dimethylformamide, 1 and 2 equivalents, respectively. To this mixture 1 equivalent of II was added with cooling. After a few minutes, the temperature was gradually increased. At about 105°C an exothermic reaction set in with evolution of hydrochloric acid. When the gas evolution had subsided, the reaction mixture was cooled and poured onto aqueous sodium acetate. After normal work-up *via* extraction with ether, an oil was isolated. Analysis (IR, NMR and GLC/MS) showed that this product was a mixture of about 85 % 3-thenyl cyanide (III) and 15 % 3-thenyl chloride (IV) produced in a total yield of about 80 %. An analogous result was obtained when the same reaction was carried out with β-phenylnitroethane. In this case benzyl cyanide was the main product (identified by IR and GLC through comparison with an authentic sample). Interestingly enough, the reaction failed when