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On the Crystal Structure of $K_3Mn(CN)_5NO \cdot 2H_2O$

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The crystal structure of $K_3Mn(CN)_5NO \cdot 2H_2O$ has been determined by single crystal Weissenberg methods. The unit cell dimensions are $a = 17.778 \pm 0.004$ Å, $b = 7.050 \pm 0.003$ Å, $c = 11.486 \pm 0.003$ Å, and $\beta = 118.61 \pm 0.01°$, the space group being No. 9 *Cc*. The structure is composed of potassium ions and complex ions of formula $Mn(CN)_5NO^{3-}$ to which water molecules are attached by hydrogen bonds. The coordination polyhedron surrounding the central manganese atom is a severely distorted octahedron, the Mn—NO distance being only 1.66 Å as compared to the mean Mn—CN distance of 1.98 Å.

The mode of coordination of the nitrosyl group in transition metal complexes has been the object of considerable discussion in recent years. An extensive programme of research into the crystal structures of the transition metal nitrosyls has therefore been started at this Department. A series of pentacyanonitrosyl metal ions are among those compounds which have been studied, the structure of the first member, $K_3Cr(CN)_5NO$, having been determined by Vannerberg.[1] The structure of $K_3Mn(CN)_5NO \cdot 2H_2O$ has now also been determined.

PREPARATION AND ANALYSIS OF $K_3Mn(CN)_5NO \cdot 2H_2O$

Manchot and Schmid [2] first prepared the compound in poor yield in 1926 by passing nitric oxide into a solution containing manganese(II) ion and potassium cyanide. An improved yield was obtained in 1941 by Blanchard and Magnusson [3] by the addition of KOH to the reaction mixture. In 1948 Hieber, Nast and Proeschel [4] reported an alternative method of preparation, whereby $K_3Mn(CN)_6$ is treated with a basic solution of hydroxylamine. This method was modified by Cotton, Monchamp, Henry and Young [5] in 1959 to give an 85 % yield of very pure substance. The same method has been used to prepare crystals for this structure investigation, the product being recrystallised in order to provide single crystals suitable for Weissenberg methods.

The compound was analysed for manganese and cyanide, *manganese* being titrated with EDTA at pH = 10 using Eriochrom-Black T as indicator, and *cyanide* determined gravimetrically as AgCN. (Found: Mn 14.90; CN 34.41. Calc.: Mn 14.91; CN 35.32).

$K_3Mn(CN)_5NO \cdot 2H_2O$ may be dehydrated by storing over P_2O_5 *in vacuo*. (Found: Mn 16.51; CN 38.05. Calc.: Mn 16.53; CN 39.14).

SPACE GROUP AND UNIT CELL

Reflections were found to be absent when

hkl : $h + k = 2n + 1$
$h0l$: $l = 2n + 1$

which is in accordance with the monoclinic space groups No. 15 $C2/c$ and No. 9 Cc. Preliminary calculations were based on the centrosymmetric space group, but it soon became obvious that a satisfactory structure determination could only be based on space group Cc.

Accurate cell dimensions were determined from Guinier powder photographs, using KCl as an internal standard ($CuK\alpha_1$ radiation, $\lambda = 1.54050$ Å, $a_{KCl} = 6.2919_4$ Å at 20°C).[6] 32 reflections were indexed with the Algol Programme Xalg Powder [7] and the same programme was used to refine the cell constants. The cell dimensions thus obtained were

Table 1. Observed and calculated values of $\sin^2\theta$ and corresponding intensities for 32 reflections recorded by Guinier powder methods.

h	k	l	$10^5 \sin^2\theta$ obs	$10^5 \sin^2\theta$ calc	I_{obs}	I_{calc}
2	0	0	976	974	vw	47
1	1	0	1439	1437	m	103
1	1	−1	1661	1660	vvw	22
2	0	−2	1864	1864	w	34
1	1	1	2385	2382	vvw	20
1	1	−2	3053	3050	w	45
3	1	0	3398	3386	vvw	13
3	1	−2	3559	3553	s	144
4	0	0	3910	3897	w	67
1	1	2	4505	4494	m	118
2	0	2	4766	4753	vvw	7
3	1	1	5055	5053	vvw	8
0	2	−1	5375	5358	vw	24
2	2	0	5763	5749	vvw	19
5	1	−3	7123	7118	m	95
2	0	−4	7425	7422	w	46
1	1	3	7780	7772	m	108
4	2	−1	7817	7811	m	84
3	1	2	7888	7887	w	43
3	1	−4	8391	8389	vw	27
4	2	0	8677	8672	m	86
6	0	0	8776	8767	vw	15
1	1	−4	9330	9329	vvw	11
5	1	−4	9402	9397	vvw	16
6	0	−4	9443	9438	vw	31
5	1	1	9678	9672	vvw	13
7	1	−2	10420	10407	vw	28
4	2	1	10697	10700	vvw	13
7	1	−3	10805	10797	vvw	16
1	3	−2	12603	12599	m	74
2	0	4	13220	13199	w	14
5	1	2	13220	13228	w	25

$a = 17.778 \pm 0.004$ Å
$b = 7.050 \pm 0.003$ Å
$c = 11.486 \pm 0.003$ Å
$\beta = 118.61 \pm 0.01°$
$V = 1263.8$ Å^3

Observed and calculated values of $\sin^2 \theta$ and the corresponding intensities of the reflections are listed in Table 1.

The density found experimentally was 1.9 g/cm^3, indicating four formula units per unit cell. The calculated density is 1.93 g/cm^3.

STRUCTURE DETERMINATION

The layers $h0l - h7l$ and $hk0 - hk5$ were registered according to the single crystal Weissenberg method, using multiple film techniques. The relative intensities of the reflections were estimated visually by comparison with a standard scale and corrected for Lorentz' and polarisation effects.

An approximate structure determination was first performed using the $hk0 - hk5$ data, which were recorded with Cu$K\alpha$ radiation. In order to index the reflections obtained by rotation around the c axis it was convenient to know the monoclinic angle β. Another crystal was therefore rotated around the b axis and the layers $h0l - h4l$ were recorded with Cu$K\alpha$ radiation. These photographs were, however, not of sufficiently high quality for accurate intensity measurements, but sufficed to determine β and to help in the approximate scaling together of the intensities obtained from rotation around the c axis.

A "three-dimensional" Patterson synthesis based on the data from the c axis yielded the following strongest peaks.

u	v	w	Peak height (arbitrary units)
0.00	0.03	0.50	1220
0.50	0.47	0.50	1220
0.50	0.03	0.23	940
0.50	0.03	0.77	940
0.00	0.47	0.23	940
0.00	0.47	0.77	940

The four manganese atoms were preliminarily assigned the position $C2/c$:4(a) and four of the potassium atoms were assigned the position $C2/c$: 4(e) with $y = 0.5$.

A "three-dimensional" Fourier synthesis based on these positions revealed the positions of the other eight potassium atoms, and a structure factor calculation with assigned isotropic temperature factors of 3.5 for all atoms gave an R value of 0.41. A second Fourier synthesis based on the manganese and potassium positions revealed the positions of all the remaining atoms, the

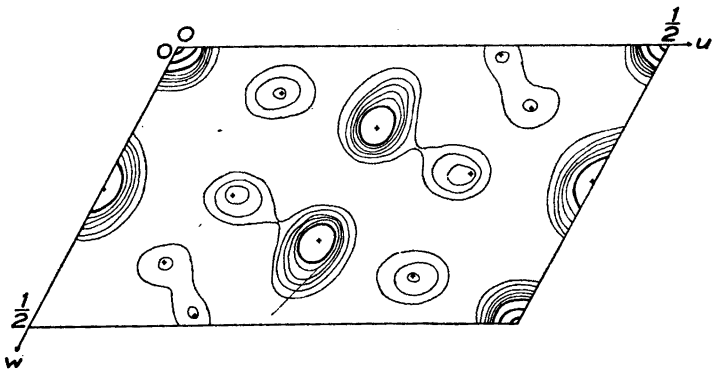

Fig. 1. Vector density projection of $K_3Mn(CN)_5NO \cdot 2H_2O$ along [010]. Each heavy line is equivalent to five fine lines.

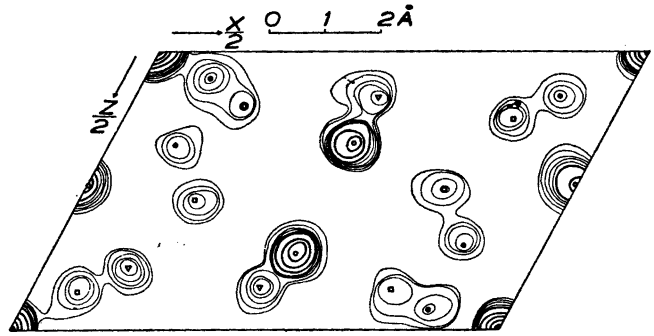

Fig. 2. Electron density projection of $K_3Mn(CN)_5NO \cdot 2H_2O$ along [010]. Heavy and fine lines represent contours of 10e/Å^2 and 2e/Å^2, respectively.

corresponding R value being 0.28. The nitrosyl groups could not be identified at this stage and were therefore treated as cyanide groups.

It was obvious that, if a statistical arrangement is excluded, the manganese atoms could not occupy centres of symmetry since each manganese atom was known to be surrrounded by an asymmetric arrangement of five cyanide groups and one nitrosyl group. The space group *Cc* was therefore adopted.

After a few cycles of isotropic least squares refinement a calculation of bond distances and angles revealed five cyanide groups at approximately equal distances and, as expected,[8,9] one group at a considerably shorter distance around each manganese atom. The atoms of this group were labelled nitrogen and oxygen.

At this stage a new set of data, obtained by rotating another crystal around the *b* axis, was available. The layers $h0l$ — $h7l$ were registered with

Mo$K\alpha$ radiation using Zr filters. No absorption corrections were applied owing to the low value of the linear absorption coefficient (20.63 cm^{-1}) and the small size of the crystal.

Table 2. Positional and thermal parameters of the atoms including their standard deviations.

Atom	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
Mn	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
K(1)	0.25080	0.13936	0.36246	0.00025	0.00052	0.00038
K(2)	0.24752	0.35949	0.66831	0.00024	0.00055	0.00037
K(3)	0.49315	0.03635	0.23752	0.00038	0.00056	0.00059
C(1)	0.41410	0.36819	0.34008	0.00084	0.00219	0.00133
C(2)	0.07583	0.11451	0.67357	0.00095	0.00215	0.00145
C(3)	0.43705	0.37243	0.58432	0.00079	0.00212	0.00124
C(4)	0.07117	0.23079	0.05564	0.00084	0.00214	0.00149
C(5)	0.41759	0.28523	0.95866	0.00087	0.00211	0.00149
N(1)	0.36452	0.28600	0.24960	0.00107	0.00248	0.00167
N(2)	0.12486	0.18800	0.77426	0.00086	0.00214	0.00136
N(3)	0.39417	0.29241	0.61906	0.00094	0.00233	0.00153
N(4)	0.11496	0.36628	0.09395	0.00126	0.00278	0.00226
N(5)	0.37176	0.16115	0.93830	0.00115	0.00247	0.00178
N(6)	0.05115	0.11502	0.43332	0.00082	0.00201	0.00129
O(1)	0.24275	0.01632	0.08504	0.00085	0.00179	0.00134
O(2)	0.23839	0.48348	0.93180	0.00088	0.00204	0.00149
O(3)	0.08814	0.21253	0.39060	0.00073	0.00186	0.00117
Vibrations						
Mn	0.01363	0.01922	0.02042	0.00268	0.00392	−0.00157
K(1)	0.02719	0.02786	0.02648	−0.00145	0.01383	0.00112
K(2)	0.02938	0.03196	0.02537	0.00136	0.01427	0.00478
K(3)	0.04237	0.02772	0.06815	−0.00248	0.01709	−0.00068
C(1)	0.01229	0.03400	0.02233	−0.00230	0.00779	−0.00261
C(2)	0.01743	0.02131	0.02499	−0.00366	0.00501	−0.00117
C(3)	0.01477	0.02842	0.01379	0.00447	0.00042	0.00194
C(4)	0.01343	0.02765	0.03492	0.00078	0.01379	−0.00033
C(5)	0.02026	0.02148	0.02911	0.00872	0.01082	0.00425
N(1)	0.04314	0.03299	0.04063	−0.00487	0.01659	−0.00865
N(2)	0.01938	0.03980	0.02402	−0.00139	0.00437	−0.00072
N(3)	0.02496	0.03651	0.03822	−0.00009	0.01183	−0.00084
N(4)	0.04211	0.03953	0.08105	−0.01165	0.03498	−0.00894
N(5)	0.04083	0.03516	0.04714	−0.00438	0.01578	−0.01161
N(6)	0.02142	0.03185	0.02165	0.00054	0.00811	0.00278
O(1)	0.02426	0.03225	0.04506	−0.00307	0.01618	−0.00404
O(2)	0.03429	0.03874	0.04094	0.00395	0.01854	0.00304
O(3)	0.02059	0.03972	0.03169	0.00788	0.01020	−0.00062

Since absorption errors were known to be much smaller for these data, the two sets of structure factors were not combined.

A structure factor calculation was based on these new data and the refined positions and isotropic temperature factors previously obtained. From the F_c/F_o fractions of the different layers of the b axis, the layer scale factors could be calculated, and the parameters obtained from the c axis data were refined isotropically with the new data. The R value converged to 0.093.

Table 3. Interatomic distances with their standard deviations.

Bond	$L \pm \sigma$(Å)	Bond	$L \pm \sigma$(Å)
Mn—C(1)	1.97 ± 0.01	K(2)—N(4)	2.85 ± 0.02
Mn—C(2)	1.97 ± 0.02	K(2)—N(5)	3.15 ± 0.02
Mn—C(3)	2.01 ± 0.01	K(2)—O(1)	2.80 ± 0.01
Mn—C(4)	1.97 ± 0.02	K(2)—O(2)	2.87 ± 0.02
Mn—C(5)	2.00 ± 0.01	K(2)—O(2)	3.23 ± 0.02
Mn—N(6)	1.66 ± 0.01	K(2)—O(3)	3.26 ± 0.01
N(1)—C(1)	1.15 ± 0.02	O(2)—N(2)	2.86 ± 0.02
N(2)—C(2)	1.18 ± 0.02	O(2)—O(3)	3.28 ± 0.02
N(3)—C(3)	1.16 ± 0.02	O(2)—N(3)	3.01 ± 0.02
N(4)—C(4)	1.18 ± 0.02	O(1)—N(3)	3.34 ± 0.02
N(5)—C(5)	1.14 ± 0.02	O(1)—O(3)	3.04 ± 0.02
N(6)—O(3)	1.21 ± 0.02	O(1)—N(1)	2.82 ± 0.02
K(1)—N(1)	3.06 ± 0.02	K(3)—C(1)	3.23 ± 0.02
K(1)—N(2)	3.03 ± 0.02	K(3)—C(2)	3.13 ± 0.02
K(1)—N(3)	3.03 ± 0.02	K(3)—C(3)	3.27 ± 0.02
K(1)—N(4)	3.28 ± 0.02	K(3)—C(4)	3.62 ± 0.01
K(1)—N(5)	2.84 ± 0.02	K(3)—C(5)	3.32 ± 0.02
K(1)—O(1)	2.85 ± 0.01	K(3)—N(1)	2.94 ± 0.02
K(1)—O(1)	3.24 ± 0.01	K(3)—N(2)	2.91 ± 0.02
K(1)—O(2)	2.82 ± 0.02	K(3)—N(3)	2.83 ± 0.02
K(1)—O(3)	3.10 ± 0.01	K(3)—N(4)	3.50 ± 0.02
K(2)—N(1)	3.10 ± 0.02	K(3)—N(5)	3.18 ± 0.02
K(2)—N(2)	3.20 ± 0.01	K(3)—N(6)	3.57 ± 0.02
K(2)—N(3)	2.96 ± 0.02	K(3)—O(3)	2.88 ± 0.01

Table 4. Angles with their standard deviations.

Angle	$\theta \pm \sigma°$	Angle	$\theta \pm \sigma°$
C(1)—Mn—C(2)	170.9 ± 0.6	Mn—C(1)—N(1)	177.6 ± 1.5
C(1)—Mn—C(3)	82.9 ± 0.5	Mn—C(2)—N(2)	175.4 ± 1.3
C(1)—Mn—C(4)	90.2 ± 0.6	Mn—C(3)—N(3)	172.5 ± 1.2
C(1)—Mn—C(5)	89.0 ± 0.6	Mn—C(4)—N(4)	177.4 ± 1.6
C(1)—Mn—N(6)	98.7 ± 0.6	Mn—C(5)—N(5)	178.3 ± 1.5
C(2)—Mn—C(3)	88.0 ± 0.6	Mn—N(6)—O(3)	174.3 ± 1.3
C(2)—Mn—C(4)	89.3 ± 0.6	O(1)—K(1)—O(2)	124.0 ± 0.4
C(2)—Mn—C(5)	89.9 ± 0.6	O(1)—K(1)—O(2)	93.8 ± 0.4
C(2)—Mn—N(6)	90.4 ± 0.6	O(1)—K(1)—O(1)	141.5 ± 0.2
C(3)—Mn—C(4)	83.9 ± 0.6	O(1)—K(2)—O(2)	124.7 ± 0.4
C(3)—Mn—C(5)	86.5 ± 0.6	O(1)—K(2)—O(2)	93.6 ± 0.4
C(3)—Mn—N(6)	177.2 ± 0.6	O(2)—K(2)—O(2)	141.2 ± 0.2
C(4)—Mn—C(5)	170.4 ± 0.6	N(1)—O(1)—N(3)	92.5 ± 0.6
C(4)—Mn—N(6)	98.3 ± 0.6	N(2)—O(2)—O(3)	96.1 ± 0.5
C(5)—Mn—N(6)	91.2 ± 0.6	N(1)—O(1)—O(3)	169.3 ± 0.7
		N(2)—O(2)—N(3)	164.0 ± 0.7

Three cycles of refinement with anisotropic thermal parameters assigned to all atoms gave an R value of 0.072.

The data were such that it was possible to distinguish the position of the nitrosyl group unequivocally. Thus the NO group and the diametrically opposite CN group were interchanged, whereupon the temperature coefficients for the atoms which were assumed to be N(6) and O(3) but were in reality C(3) and N(3) increased, whereas those for the atoms assumed to be C(3) and

Table 5. Observed and calculated structure factors for $K_3Mn(CN)_5NO \cdot 2H_2O$.

h	k	l	Fobs	Fcalc	h	k	l	Fobs	Fcalc	h	k	l	Fobs	Fcalc	h	k	l	Fobs	Fcalc	h	k	l	Fobs	Fcalc
2	0	0	6092	6760	15	-1	-1	3195	2860	17	-1	-9	3925	4051	16	-2	-8	3937	3551	9	-3	-8	4721	4595
4	0	0	16277	17388	13	-1	-1	2884	1870	15	-1	-9	2724	2092	14	-2	-8	4700	4838	7	-3	-8	3001	3061
6	0	0	12912	12448	11	-1	-1	2325	1751	11	-1	-9	5502	5184	12	-2	-8	5049	4720	5	-3	-8	6522	6557
8	0	0	19208	21627	7	-1	-1	6609	6455	9	-1	-9	4936	4710	10	-2	-8	5998	5709	3	-3	-8	2561	2268
12	0	0	12340	13808	5	-1	-1	5431	5063	5	-1	-9	2489	2031	8	-2	-8	4703	5100	1	-3	-8	4095	4075
16	0	0	9274	9473	3	-1	-1	2853	3154	3	-1	-9	4388	4043	6	-2	-8	7084	7147	1	3	8	1868	1985
20	0	0	4443	4164	1	-1	1	4703	5138	1	-1	-9	3334	3502	4	-2	-8	4462	4504	3	3	8	6982	7805
24	0	0	4504	3860	3	1	1	4976	4835	21	-1	-10	2805	3134	2	-2	-8	5222	4740	11	3	8	3028	3079
22	0	-2	2968	2908	5	1	1	8197	8945	19	-1	-10	3028	2757	0	2	8	4238	3491	15	3	8	2844	2503
18	0	-2	5782	5108	9	1	1	2904	2818	17	-1	-10	3529	3049	2	2	8	6668	6518	13	-3	-9	2541	2395
14	0	-2	4988	4741	11	1	1	4007	3522	15	-1	-10	2877	2770	4	2	8	4959	4531	11	-3	-9	2257	2328
10	0	-2	3069	2560	13	1	1	3392	3446	13	-1	-10	3392	3441	6	2	8	3228	3616	9	-3	-9	1996	1436
10	0	-2	4813	4265	23	-1	-2	2574	2463	11	-1	-10	3431	3680	12	-2	-9	4799	4203	7	-3	-9	3502	3307
8	0	-2	4007	3115	19	-1	-2	4403	4808	9	-1	-10	4041	4519	8	-2	-9	4564	4182	5	-3	-9	2955	2751
6	0	-2	3623	2879	17	-1	-2	3402	3640	7	-1	-10	5940	5365	6	-2	-9	2704	2809	3	-3	-9	2763	2254
4	0	-2	2194	1467	15	-1	-2	7618	8170	5	-1	-10	4063	4331	2	-2	-9	4947	4449	1	-3	-9	3121	2911
2	0	-2	8747	8407	13	-1	-2	5340	5587	3	-1	-10	4300	4189	0	2	10	3735	3565	23	-3	-10	2595	2173
0	0	2	5094	3896	11	-1	-2	8999	9252	1	-1	-10	3142	2921	2	-2	-10	4619	4240	21	-3	-10	2463	2357
2	0	2	6384	6556	9	-1	-2	3923	3804	1	1	10	3733	3717	4	-2	-10	3982	3972	19	-3	-10	2527	2128
4	0	2	4647	4594	7	-1	-2	11651	11776	3	1	10	2603	2645	12	-2	-10	2986	2829	17	-3	-10	2228	2341
6	0	2	4364	4589	5	-1	-2	12412	12373	5	1	10	2719	2768	14	-2	-11	3473	2919	15	-3	-10	5467	5226
10	0	2	3923	3622	3	-1	-2	16964	17880	3	1	11	2306	2413	12	-2	-11	4788	3711	13	-3	-10	3453	3273
12	0	2	3331	2936	1	-1	-2	8702	8975	17	-1	-12	2267	2351	10	-2	-11	4708	4761	11	-3	-10	4951	4716
14	0	2	2692	2684	1	1	2	15521	17939	13	-1	-12	2316	2481	6	-2	-11	4545	3265	9	-3	-10	3150	3068
22	0	-4	2873	3289	3	1	2	13176	14340	11	-1	-12	2111	1807	4	-2	-11	3143	3571	7	-3	-10	3738	3460
18	0	-4	6863	7070	5	1	2	12940	14205	5	-1	-12	2762	2764	2	-2	-11	5023	4213	5	-3	-10	3010	2830
16	0	-4	3651	3837	7	1	2	4809	5660	1	-1	-12	4072	3698	12	-2	-12	3290	3136	3	-3	-10	4391	4615
14	0	-4	10168	10153	9	1	2	8772	8961	17	-1	-13	2538	2682	14	-2	-12	3356	3003	1	-3	-10	3180	2829
12	0	-4	2788	2866	11	1	2	5450	5114	11	-1	-13	3688	3830	17	-3	0	2442	2821	1	3	10	3807	3712
10	0	-4	13780	14623	13	1	2	5968	5601	5	-1	-13	3767	4150	13	-3	0	1898	2235	5	3	10	3234	3100
8	0	-4	5979	6178	17	1	2	4000	4044	15	-1	-14	2843	2835	9	-3	0	4652	4184	17	-3	-11	2295	1622
6	0	-4	19433	19113	19	1	2	2683	2680	9	-1	-14	2344	2595	7	-3	0	6204	5958	17	-3	-12	2371	2404
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14	0	-10	2621	2622	7	-1	-6	5269	5732	4	-2	-4	9222	8435	9	3	4	3660	3648	8	4	2	2210	2362
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13	-1	0	3138	3289	5	1	8	4741	4688	6	-2	-7	3631	2532	21	-3	-8	3105	3279	12	4	4	6024	5850
15	-1	0	2993	3218	7	1	8	4721	5206	4	-2	-7	4653	4451	17	-3	-8	3417	3262	14	4	4	1845	1874
19	-1	0	2337	1893	13	1	8	3078	2823	0	2	7	2513	2128	13	-3	-8	6474	6440	16	4	4	3003	3130

Table 5. Continued.

h	k	l	Fobs	Fcalc	h	k	l	Fobs	Fcalc	h	k	l	Fobs	Fcalc	h	k	l	Fobs	Fcalc	h	k	l	Fobs	Fcalc
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8	-4	-5	5153	4902	11	-5	-1	3612	3316	21	-5	-8	2100	1905	6	-6	-3	2372	2382	0	-6	12	1764	1827
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2	-4	-5	2215	2141	5	-5	-1	7745	8125	13	-5	-8	2897	2560	0	-6	3	958	835	0	-6	14	1373	1433
0	4	5	5997	5510	3	-5	-1	10490	911	11	-5	-8	1757	1593	2	-6	3	1368	1609	15	-7	0	1980	2107
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4	4	5	1204	1216	3	5	1	5391	5452	7	-5	-8	1548	1428	6	-6	3	1592	1784	11	-7	0	2424	2355
8	4	5	4003	4039	5	5	1	3029	2786	5	-5	-8	1547	1430	10	-6	3	990	1046	9	-7	0	2081	1316
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24	-4	-6	1543	1888	9	5	1	1031	1092	1	-5	-8	4673	4274	22	-6	-4	1678	1809	5	-7	0	4015	4076
22	-4	-6	2510	2598	11	5	1	4416	4312	1	5	8	3890	2931	18	-6	-4	2424	2489	3	-7	0	3799	4202
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14	-4	-6	5651	5530	21	-5	-2	2252	2610	7	5	8	2437	2450	12	-6	-4	1646	1828	7	-7	-1	1458	1309
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6	-4	-8	3659	3886	1	5	3	3877	3800	9	5	10	1677	2150	24	-6	-6	1465	1791	13	-7	-4	4385	4057
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18	-4	-9	1476	1397	17	-5	-4	2683	2543	13	-5	-12	1869	1742	0	-6	-6	3257	3201	7	7	4	3812	3531
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4	4	12	2532	2709	3	-5	-6	7588	6911	8	6	1	3331	1962	16	-6	-10	1382	1617	9	7	8	2433	2559
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16	-4	-14	1988	1764	1	5	6	3056	2908	22	-6	-2	1891	1772	12	-6	-10	1057	1190	21	-7	-10	1490	1354
12	-4	-14	1499	1333	3	5	6	2951	2917	18	-6	-2	2102	2084	10	-6	-10	2131	2153	13	-7	-10	1262	1670
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14	-4	-16	1646	2014	23	-5	-7	2114	1796	8	-6	-2	3281	2973	0	-6	10	1320	1348	1	-7	-10	1982	1928
12	-4	-16	1690	1839	19	-5	-7	1834	1798	6	-6	-2	3750	3456	18	-6	-11	1552	1524	1	7	10	1496	1468
10	-4	-16	1644	1902	17	-5	-7	1214	1294	4	-6	-2	2206	2536	20	-6	-12	1371	1582	5	7	10	1451	1358
8	-4	-16	1790	1614	15	-5	-7	3491	3490	2	-6	-2	2910	3505	16	-6	-11	1514	1966	15	-7	-12	1402	1206
6	-4	-16	1680	1605	13	-5	-7	987	1102	0	6	2	2911	2752	14	-6	-11	1226	1631	13	-7	-12	2415	2613
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9	-5	0	4813	4522	5	-5	-7	2124	2198	8	6	2	2841	2636	0	6	11	1522	1891	5	-7	-12	1785	1852
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15	-5	0	1823	1837	1	5	7	4420	4085	14	6	2	2019	1967	14	-6	-12	1406	1429	3	7	12	1534	1518
17	-5	0	1442	1597	3	5	7	2869	2752	16	6	2	1846	1938	12	-6	-12	1771	2100	15	-7	-14	1507	1891
										18	-6	13	1146	1148	10	-6	-12	1148	1421					

N(3), but in fact N(6) and O(3), decreased. At the same time a somewhat larger R value was obtained.

The final parameters were also used in a structure factor calculation with the c axis data, recorded with Cu$K\alpha$ radiation, giving an R value as high as 0.15, owing to severe absorption errors which were not corrected for.

The atomic parameters are given in Table 2. The most interesting bond distances and angles are given in Tables 3 and 4.

The Lorentz' and polarisation correction, the Patterson synthesis, all structure factor calculations, Fourier syntheses and least squares refinement were performed on the SAAB D21 computer at the University Computing Center, Gothenburg, using programmes written by Abrahamsson *et al.*[10–13] Bond distances and angles were calculated on the computer CD 3600 at the University Computing Center, Uppsala, using the programme DISTAN written by Zalkin and modified by Lundgren and Liminga.[14]

IR Spectra. The IR spectra of $K_3Mn(CN)_5NO{\cdot}2H_2O$ and $K_3Mn(CN)_5NO$ were recorded and found to be in agreement with those reported by Cotton *et al.*[5]

Magnetic properties. The diamagnetism of the compound reported by Cotton *et al.*[5] was confirmed.

DISCUSSION

The structure of $K_3Mn(CN)_5NO{\cdot}2H_2O$, illustrated in Fig. 3, is composed of potassium ions and complex ions of formula $Mn(CN)_5NO^{3-}$ to which water molecules are attached by hydrogen bonds.

The coordination polyhedron surrounding the central manganese atom is a distorted octahedron of point symmetry C_{4v} in which the Mn—CN bond distances vary between 1.97 and 2.01 Å and the Mn—NO bond distance is

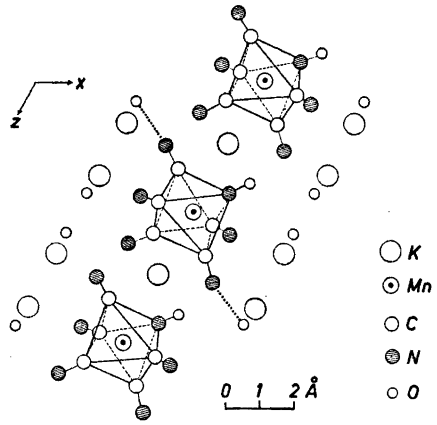

Fig. 3. Projection of the structure of $K_3Mn(CN)_5NO{\cdot}2H_2O$ along [010]. The Mn atoms lie in the [0½0] plane. Dotted lines indicate possible hydrogen bonds.

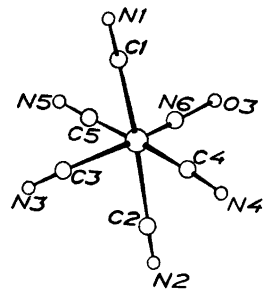

Fig. 4. The complex ion $Mn(CN)_5NO^{3-}$.

1.66 Å. The Mn—C—N and Mn—N—O bond angles are almost linear, but there are some significant deviations from 180°, the largest deviation being observed for the cyanide group opposite to the nitrosyl group. Three of the carbon atoms and the nitrogen atom of the nitrosyl group define a plane which also contains the manganese atom. The manganese atom does not, however, lie in the plane defined by the four carbon atoms C(1), C(4), C(2), and C(5), Fig. 4, but is displaced approximately 0.16 Å towards the nitrosyl group. This means that the angle between the Mn—N(6) and Mn—C bonds is greater than 90° for C(1) and C(4), *cf.* Table 4. A similar distortion has been reported for the nitroprusside ion.[15] In this structure determination, however, the N—O bond distance was found to be only 1.13 Å, which is remarkably short compared with the N—O distance found in this structure 1.21 Å.

The configuration of the complex ion is in fairly good agreement with the model suggested by Ballhausen and Gray [8,9] in which nearly all the π-bonding is axially directed. A very strong π-bond was thus expected to occur between manganese and the nitrosyl group or the diametrically opposite cyanide group. An Mn—N bond distance of 1.66 Å, which is much shorter than the sum (1.91 Å) of the covalent radii was also found, while the N—O bond distance is considerably longer (1.21 Å) than the bond distance in nitric oxide (1.14 Å). This is due to the occupation of antibonding π-orbitals of the NO group. The bond length 1.21 Å is slightly longer than the bond distance expected for a double bond (1.18 Å).

The fact that the manganese atom does not lie in the plane formed by the four carbon atoms C(1), C(4), C(2), and C(5) may be explained if the d_{xy} orbital is assumed to have an antibonding character rather than nonbonding as in the Ballhausen-Gray treatment. The Mn—C bond distances are 1.97—2.01 Å, which may be compared with the sum (1.94 Å) of the covalent radii. This somewhat larger distance can be due to the same repulsive effect.

The potassium atoms K(1) and K(2) are surrounded by four oxygen and five nitrogen atoms, in the form of a very distorted face centered trigonal prism, an idealized picture of which is shown in Fig. 5. K(3) appears to be distorted octahedrally coordinated by five CN-groups and one NO-group and thus has 12 nearest neighbours (see Table 3).

The short O(1)—N(1) and O(2)—N(2) distances, 2.82 and 2.86 Å, respectively, indicate that two of the four hydrogen atoms are located in these directions. These bind the water molecules to the complex group. The other

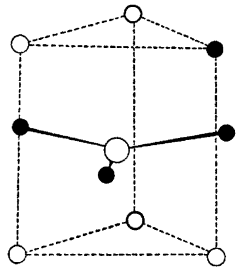

Fig. 5. The coordination polyhedron of K(1). Oxygen atoms are denoted by shaded rings.

distances from the water oxygen atoms to the NO and CN groups are such that hydrogen bonding may be suspected to occur also for the two remaining hydrogen atoms. Thus the distances O(1)—O(3) and O(2)—N(3) are 3.04 Å and 3.01 Å. A "three-dimensional" Fourier $|F_o - F_c|$ synthesis also shows indications of peaks attributable to hydrogen atoms in these directions. IR data also suggest that the nitrosyl group participates in hydrogen bonding.[5]

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