Contribution of the Chemical Laboratory IV, Universitetsparken 5,
DK-2100 Copenhagen Ø, Denmark. Institute of Inorganic Chemistry,
Freiestrasse, 3, CH-3000 Bern 9, Switzerland.

The Crystal Structure of Manganese(II) Hexacyanochromate(III), $Mn_3[Cr(CN)_6]_2.xH_2O$

H.U. Güdel,[a] H. Stucki,[b] and A. Ludi[b,c]

Received June 5, 1972

The crystal structure of $Mn_3[Cr(CN)_6]_2.xH_2O$ has been determined from three dimensional X-ray diffraction data measured by counter methods. The cubic face centered unit cell with space group O^3–F432 or O_h^5–Fm3m has a = 10.761(4) Å and contains 1⅓ formula units, the measured and calculated densities are 1.50 and 1.48 g/cm³, respectively. The structure was determined by application of a general structural model for Prussian Blue analog compounds. Least squares refinement of the positional and individual isotropic thermal parameters led to a final R value for the observed reflections of 0.054.

The crystal structure is very closely related to the structures of other Prussian Blue analog compounds. Manganese and chromium atoms occupy the positions 4a (0 0,0) and 4b (0.5, 0.5, 0.5), respectively, of the unit cell. Carbon and nitrogen atoms are situated at positions 24e (x,0,0) and two different kinds of oxygen atoms (O(1) and O(2)) are distributed in general positions with O(1) (coordinated water) close to the nitrogen position and O(2) (zeolitic water) close to the special position 8c (0.25, 0.25, 0.25). One third of all $Cr(CN)_6$ groups are statistically absent so that each manganese atom has a mixed coordination, its average composition being MnN_4O_2. All cyanide groups are bridged between chromium and manganese atoms, with the carbon atoms bonded to chromium. The Cr-C, C-N, Mn-N, and Mn-O(1) distances are 2.06(1), 1.12(2), 2.20(1), and 2.36(4) Å respectively.

Introduction

The crystal structure of $Mn_3[Cr(CN)_6]_2 . xH_2O$ has been described in terms of a structural model developed for Prussian Blue by Keggin and Miles.[1,2] Recent single crystal studies of various polynuclear transition metal cyanides led to a modification of the model.[3-6]

Since numerous crystalline transition metal cyanides exhibit simple X-ray diffraction powder patterns corresponding to cubic unit cells with lattice constants between 9.9 Å and 10.9 Å,[6-7] their crystal structures may be assumed to be closely related.

In a series of compounds of the general formula $M_3[Co(CN)_6]_2 . xH_2O$ (M = divalent transition metal or metal of Class B) it had been found that with the diffusion technique employed the biggest crystals, suitable for single crystal X-ray diffraction studies, could be grown with Cd^{2+} and Mn^{2+}.[3] The same trends were expected in the series of compounds $M_3[Cr(CN)_6]_2.xH_2O$.

It was the purpose of the present study to grow single crystals of $Mn_3[Cr(CN)_6]_2.xH_2O$ and subsequently, to determine if the modified structural model for Prussian Blue analogs can also be applied to this crystal structure. Interatomic distances should emerge and be comparable with those found in other transition metal cyanides.

Experimental Section

$Mn_3[Cr(CN)_6]_2 . xH_2O$ was prepared by slow interdiffusion[3] of manganese(II) sulfate and tetrabutylammoniumhexacyanochromate(III) solutions.

Analysis. Calculated for $Mn_3[Cr(CN)_6]_2 . 12H_2O$: C, 18.1; N, 21.1; H, 3.0; H_2O, 27.1. Calculated for $Mn_3[Cr(CN)_6]_2 . 14H_2O$: C, 17.3; N, 20.2; H, 3.4; H_2O, 30.3. Found: C, 17.1; N, 19.7; H, 3.2; H_2O, 29.8. The water content is dependent on the humidity and the temperature. Near room temperature x lies between 12 and 15.

Unit-cell. X-ray diffraction powder photographs taken on a Guinier camera using FeKα radiation, and Weissenberg single crystal photographs taken with MoKα radiation showed that $Mn_3[Cr(CN)_6]_2 . xH_2O$ has a cubic face-centered unit cell with axial length aproximately 10.75 Å. A cube-shaped crystal with an edge length of 0.12 mm was then mounted on a Picker FACS-1 single Crystal X-ray diffractometer with a graphite monochromated

---

(a) Chemical Laboratory IV, Universitetsparken, DK-2100 Copenhagen Ø, Denmark. Nachwuchsstipendiat Schweizerischer Nationalfonds.
(b) Institute of Inorganic Chemistry, Freiestrasse 3,CH-3000 Bern 9, Switzerland.
(c) To whom correspondence should be addressed.
(1) E. Tani and E. Morisi, *Acta Cryst.*, *15*, 90 (1962).
(2) J.F. Keggin and E.D. Miles, *Nature (London)*, *137*, 577 (1936).
(3) A. Ludi, H.U. Güdel, and M. Rüegg, *Inorg. Chem.*, *9*, 2224 (1970).
(4) A. Ludi and G. Ron, Chimia, *25*, 333 (1971).
(5) H.U. Güdel, *Acta Chem. Scand.*, *26*, 2169 (1972).
(6) A. Ludi and H.U. Güdel, *Structure and Bonding*, to be published.
(7) R.W.G. Wyckoff, *Crystal Structures*, Vol. III, 2nd edition; Interscience, New York, N.Y., 1965, p. 382.

MoKα radiation source, and the lattice constant was more precisely determined using the least squares procedure which employs the diffractometer setting angles of twelve reflections.[8] The following result was obtained: a = 10.761(4) Å. The figure in parentheses is the estimated standard deviation.

Density. The density of several single cystals was measured pycnometrically (decahydronaphthalene). Corresponding densities were calculated assuming that, as predicted by the modified structural model of Prussian Blue analogs, there were $1^1/_3$ formula units in the unit cell. This assumption was shown to be correct in the subsequent structure analysis.

Results. D (calculated for x = 12): 1.42 g/cm^3; D (calculated for x = 14): 1.48 g/cm^3; D (measured): 1.50(5) g/cm^3, where the figure in parentheses is the estimated error of the measurement. In agreement with the analysis figures, these results indicate that the water content is somewhat higher than 12 molecules per formula unit.

Measurement and reduction of diffraction data: The procedure described in ref. 5 was applied. 1237 reflections, 260 of which were independent, were collected in the range $0.093 \leqslant \sin\theta/\lambda \leqslant 0.929$. Minimum and maximum transmission factors were 0.787 and 0.830 respectively. By averaging reflections that were equivalent in Laue group O_h-m3m (vide infra) an independent set of 149 observed and 111 unobserved reflections was obtained.

Space group: Weissenberg photographs exhibited the absences $h+k$, $h+\ell$, $k+\ell \neq 2n$, corresponding to a cubic face-centered unit cell. No further systematic extinctions were observed so that T^2-F23, T_h^3-Fm3, O^3-F432, T_d^2-F$\bar{4}$3m and O_h^5-Fm3m were possible space groups, the former two belonging to Laue group T_h-m3 and the latter three to O_h-m3m. To distinguish between these two classes the corrected intensities of reflections that were possibly equivalent were compared. This showed that pairs of reflections hko and kho and also hkℓ and hℓk had the same corrected intensities. The space groups with Laue group T_h-m3 could thus be excluded.[9] However, no discrimination between the three remaining space groups could be made.

Analysis of the Structure. According to the structural model used for the description of several other Prussian Blue analog compounds,[3-6] 4 manganese atoms were placed at the position 4a (0,0,0), four chromium atoms with occupation factors 2/3 were placed at position 4b (0.5, 0.5, 0.5), and 24 carbon atoms and 24 nitrogen atoms, also with occupation factors of 2/3 were assigned to the 24-fold position (x,0,0). x_C and x_N were chosen in such a way that the Mn-N and N-C distances were 2.21 Å and 1.14 Å respectively, as found in $Mn_3[Co(CN)_6]_2 . xH_2O$.[3]

The previous crystal structure analyses of Prussian Blue analog compounds[3,5] had shown that in the disordered structure oxygen atoms O(1) and O(2) occupy sites close to the vacant nitrogen positions and close to the positions (0.25, 0.25, 0.25) and (0.75, 0.75, 0.75) respectively. Structure factors only including the atoms Mn, Cr, C, and N (individual atomic isotropic temperature factors were chosen by analogy) and a difference electron density map were computed. The map showed two independent broad positive regions centered at (0.21,0,0) and (0.25, 0.25, 0.25).

The structural parameters were refined using a full matrix least squares procedure. The function minimized was $\Sigma w(|F_{obs}| - |F_{calc}|)^2$, where the summation is taken over all the observed reflections, w is the weighting function, and F_{obs} and F_{calc} are the observed and calculated structure factors respectively. The weighting function was based upon the scheme proposed by Cruickshank *et al.*,[10] the parameters being chosen in such a way that the product $w(|F_{obs}| - |F_{calc}|)^2$ was constant as a function of $\sin\theta/\lambda$. All structure factor calculations used the atomic scattering factors for Mn^{2+}, Cr, C, $N^{0.5-}$, and O tabulated by Ibers.[11] The values for $N^{0.5-}$ were obtained by interpolating between the tabulated scattering factors of N and N^-. This choice of scattering factors was based on the results of a theoretical study of various $M(CN)_6$ complexes.[12] Corrections for the real part, $\Delta f'$, of the anomalous scattering were applied where appropriate.[11] A scale factor and positional and individual atomic isotropic temperature factors were refined. Since many of the oxygen atoms in general equivalent positions were very close to each other and to the nitrogen atoms, however, there was very strong correlation of the corresponding positional and thermal parameters, so that it was not possible to refine all these parameters in the same least squares cycle. In the refinement scheme used all but one of the correlated parameters were fixed for a given run. By repeating this procedure in such a way that each parameter was free to move in at least three least-squares cycles convergence was reached.

A first refinement of the crystal structure of $Mn_3[Cr(CN)_6]_2.xH_2O$ was carried out in space group O_h^5–Fm3m with O(1) restricted to the 24-fold special position (x,0,0) (occupation factor 1/3) and (O(2) to the 8-fold special position (0.25,0.25,0.25). The final reliability factors were R = 0.069 and RW = 0.113, where the normal reliability factor is defined as $R = \Sigma||F_{obs}|-|F_{calc}||/\Sigma|F_{obs}|$, and the weighted reliability factor is $RW = (\Sigma w(|F_{obs}| - |F_{calc}|)^2/\Sigma w F_{obs}^2)^{1/2}$, the summation being taken over all observed reflections. O(1) and O(2) had high temperature factors of 11.1 Å^2 and 22.2 Å^2 respectively.

O(1) and O(2) were subsequently placed at general positions near to these special sites, and the structure was refined both in O^3–F432 and O_h^5–Fm3m. No attempt of a refinement in space group T_d^2–F$\bar{4}$3m was made. The special positions (0.25,0.25,0.25) and (0.75,0.75,0.75) are not equivalent in this space group. Therefore, eight oxygen atoms O(2) ought to be statistically distributed on two independent sets of

---

[8] W.R. Busing and H.A. Levy, *Acta Cryst.*, *22*, 457 (1967).

[9] N.F.M. Henry and K. Lonsdale (Eds.), *International Table for X-Ray Crystallography*, Vol. I, Kynoch Press, Birmingham, 1952.

[10] D.W.J. Cruickshank, D.E. Pilling, A. Bujosa, F.M. Lowell, and M.R. Truter, *Computing Methods and the Phase Problem in X-Ray Crystal Analysis*, Pergamon Press, Oxford, 1961, p. 32.

[11] C.H. McGillavry and G.R. Rieck (Eds.), *International Tables for X-Ray Crystallography*, Vol. III, Kynoch Press, Birmingham, 1962, Tables 3.3.1A, p. 202, 3.3.1B, p. 210 and 3.3.2C, p. 215.

[12] P. Millie and A. Veillard, *J. Chim. Phys.*, *62*, 20 (1965).

96-fold positions near to these sites. Such a description was considered to be too artificial.

The final reliability factors were R = 0.054 and RW = 0.071 in O^3–F432 and R = 0.055 and RW

Table I. Final structural parameters of $Mn_3[Cr(CN)_6]_2 \cdot xH_2O$ from the refinement in space group O_h^5-Fm3m. The estimated standard deviations of the parameters ($\times 10^4$ for coordinates, $\times 10^2$ for thermal parameters) are given in parentheses.

	x/a	y/b	z/c	B
Mn	0	0	0	2.20(05)
Cr	0.5	0	0	1.84(05)
C	0.3083(10)	0	0	3.14(15)
N	0.2040(12)	0	0	4.17(18)
O(1)	0.2112(33)	0.0498(35)	0.0309(31)	4.04(70)
O(2)	0.2041(66)	0.2079(55)	0.2654(50)	10.23(183)

Table II. Observed structure amplitudes, $|F_{obs}|$, and calculated structure factors, F_{calc} (in electrons). The calculated values are those from the refinement in space group O_h^5-Fm3m. Within each group of reflections with constant h and k the columns list, from left to right, ℓ, 10 $|F_{osb}|$, 10 F_{calc}. An unobserved reflection is marked by an asterisk.

0,0,L		
2	1679	1859
4	2317	2534
6	1592	1464
8	786	781
10	754	741
12	344	375
14	300	306
16	206	209
18	102	126
20	116	91
0,2,L		
2	1303	1273
4	1246	1210
6	1032	1022
8	525	555
10	613	572
12	273	296
14	245	244
16	192	172
18	90	104
0,4,L		
4	1607	1517
6	1019	1046
8	563	593
10	622	581
12	285	313
14	239	250
16	187	178
18	94	107
0,6,L		
6	898	844
8	510	530
10	494	500
12	273	296
14	221	226
16	171	164
18	84	98
0,8,L		
8	320	338
10	332	344
12	189	211
14	157	163
16	127	124
18	59*	75
0,10,L		
10	323	320
12	192	210
14	146	156
16	115	117
0,12,L		
12	132	142
14	101	107
16	71*	83
0,14,L		
14	88	82
1,1,L		
1	398	406
3	312	217
5	386	348
7	31*	55
9	164	158
11	26*	20
13	36*	47
15	43*	20
17	47*	2
19	33*	11
1,3,L		
3	29*	108
5	291	277
7	86	75
9	149	168
11	27*	44
13	53*	62
15	40*	29
17	23*	9
19	50*	14
1,5,L		
5	228	209
7	73	84
9	99	95
11	24*	11
13	32*	32
15	30*	10
17	25*	1
19	36*	7
1,7,L		
7	17*	67
9	71	84
11	30*	27
13	44*	40
15	24*	14
17	30*	5
1,9,L		
9	65*	63
11	27*	23
13	39*	31
15	20*	11
17	34*	5
1,11,L		
11	20*	2
13	27*	13
15	23*	0
1,13,L		
13	20*	17
15	26*	5
2,2,L		
2	473	-397
4	686	720
6	566	556
8	296	313
10	475	440
12	202	209
14	206	186
16	169	135
18	67*	82
2,4,L		
4	808	835
6	749	711
8	395	402
10	473	437
12	226	233
14	205	193
16	165	144
18	71*	87
2,6,L		
6	605	598
8	359	355
10	419	384
12	212	217
14	182	175
16	148	133
18	68*	80
2,8,L		
8	220	214
10	272	248
12	152	147
14	135	121
16	118	99
18	61*	61
2,10,L		
10	271	248
12	161	160
14	131	124
16	98	98
2,12,L		
12	112	107
14	87	86
2,14,L		
14	71*	69
3,3,L		
3	209	137
5	201	188
7	36*	119
9	181	164
11	61*	64
13	47*	72
15	50*	36
17	20*	15
19	35*	16
3,5,L		
5	183	211
7	71	79
9	105	111
11	18*	26
13	24*	43
15	35*	17
17	27*	6
19	23*	9
3,7,L		
7	79	87
9	84	85
11	23*	35
13	52*	44
15	33*	18
17	24*	9
3,9,L		
9	74	71
11	44*	29
13	25*	35
15	34*	15
17	27*	8
3,11,L		
11	30*	7
13	36*	16
15	22*	3
3,13,L		
13	33*	19
4,4,L		
4	962	999
6	808	766
8	451	449
10	468	457
12	241	255
14	204	204
16	166	151
18	81*	91
4,6,L		
6	633	639
8	391	403
10	413	399
12	221	238
14	182	185
16	146	138
18	73*	84
4,8,L		
8	243	256
10	281	273
12	156	168
14	135	134
16	108	105
4,10,L		
10	[illegible]97	265
12	170	173
14	131	132
16	103	100
4,12,L		
12	115	116
14	92	91
5,5,L		
5	130	113
7	54*	78
9	53*	65
11	19*	9
13	20*	25
15	24*	6
17	30*	0
5,7,L		
7	40*	48
9	48*	61
11	29*	15
13	19*	28
15	26*	8
17	33*	3
5,9,L		
9	29*	52
11	25*	18
13	30*	26
15	34*	8
17	21*	3
5,11,L		
11	26*	-2
13	30*	8
15	26*	-1
5,13,L		
13	21*	13
6,6,L		
6	570	546
8	349	356
10	354	351
12	208	216
14	169	167
16	126	126
18	79*	77
6,8,L		
8	237	231
10	244	245
12	152	152
14	122	122
16	102	95
6,10,L		
10	239	238
12	148	156
14	108	121
16	84	91
6,12,L		
12	105	104
14	76	83
7,7,L		
7	16*	48
9	29*	47
11	22*	13
13	33*	24
15	33*	8
17	20*	4
7,9,L		
9	39*	46
11	19*	15
13	33*	23
15	22*	8
7,11,L		
11	31*	-3
13	20*	7
15	27*	0
7,13,L		
13	25*	12
8,8,L		
8	159	147
10	174	170
12	108	106
14	95	90
16	80*	72
8,10,L		
10	171	175
12	113	115
14	90	92
8,12,L		
12	76*	77
9,9,L		
9	27*	45
11	20*	18
13	41*	22
15	22*	9
9,11,L		
11	21*	2
13	28*	5
10,10,L		
10	165	169
12	105	114
14	86*	85
10,12,L		
12	58*	78
11,11,L		
11	56*	-7

= 0.073 in O_h^5–Fm3m. They are significantly lower than the factors obtained with restrictions on the positional parameters of O(1) and O(2). From a merely crystallographic point of view it is surprising that the oxygen atoms do not occupy the special positions, but, instead, are statistically distributed on general positions, thus leading to a disordered structure. It becomes, however, understandable from a chemical point of view. The oxygen atoms O(1) belong to the coordination unit of the manganese atoms. The oxygen atoms O(2) are of water molecules with typical zeolitic character. They are most probably bonded by hydrogen bridges to the oxygen atoms O(1). Oxygen-oxygen distances in most hydrogen bonded systems have been found to lie in a range of 2.50 Å - 3.00 Å.[13] Since the distance O(1) - O(2) with both oxygen atoms restricted to the special positions would be 3.83 Å in $Mn_3[Cr(CN)_6]_2.xH_2O$, it becomes clear that they have to move out of these sites in order to form hydrogen bonds.

All final parameters of the two refinement in O^3–F432 and O_h^5–Fm3m differ by less than one estimated standard deviation. That both refinements lead to almost equally good agreement between observed and calculated structure amplitudes is understandable since both O(1) and O(2) occupy sites very close to the special position (x,x,y) (Table I), and this has the same multiplicity in both O^3-F432 and O_h^5-Fm3m. The results of the refinement in O_h^5-Fm3m are given in Tables I - III.

Discussion

The crystal structure of $Mn_3[Cr(CN)_6]_2 . xH_2O$ is very closely related to the structures of other Prussian Blue analog compounds.[6] The $Cr(CN)_6$ ions centered at the position 4b are, by symmetry, perfectly regular octahedra. The incomplete occupancy arises from the absence of whole units. The manganese atoms have a mixed nitrogen and oxygen (O(1)) coordination of the average composition MnN_4O_2. Thus, though the point symmetry of the positions 4a is also m3m,[9] due to the statistical absence of $Cr(CN)_6$ units the actual microsymmetry at the points occupied by the manganese atoms is lower. All the cyanide groups act as bridges between manganese and chromium atoms in the three dimensional framework, with the carbon atom always pointing towards the chromium.

The water molecules (O(1)) coordinated to manganese are responsible for the interruptions in the network. These interruptions are considered to occur completely at random, thus leading to a statistically disordered structure.

The water molecules (O(2)) located in the cavities of the cubic network are relatively free, probably being attached by hydrogen bonds to the coordinated atoms O(1). The O(1) - O(2) interatomic distances (Table III) agree well with oxygen-oxygen distances in other systems that do form such hydrogen bonds.[13] The high thermal parameters obtained for O(2) in the least squares refinement and the fact that the compound, like most of the Prussian Blue analog compounds,[6] loses part of its water on heating without marked changes in its unit cell dimensions is consistent with the presence of zeolitic water molecules (O(2)) occupying the cavities of the three dimensional network and being held within this network by relatively weak forces.

Table III. Some interatomic distances (in Å) in $Mn_3[Cr(CN)_6]_2 . xH_2O$. The figures are those from the refinement in space group O_h^5-Fm3m. The four shortest O(1) - O(2) distances are given. The figures in parantheses are estimated standard deviations (× 10^3).

Mn-N	2.195(12)
Cr-C	2.063(11)
C-N	1.123(17)
Mn-O(1)	2.359(36)
O(1)-O(2)	2.589(78)
	2.598(77)
	2.861(75)
	2.884(74)

Chemical analysis and the measured density indicate that the number of water molecules is between 13 and 15, rather than 12 as assumed in this crystal structure determination. Although a difference electron density map did not show any significant positive peaks that could be assigned to oxygen atoms, the possible presence of additional water of hydration cannot be ruled out. The number of electrons in the oxygen atoms possibly not accounted for is only about three percent of the total number of electrons in the unit cell. Furthermore, if these atoms statistically occupy 96- or 192-fold general positions, the electron density at anyone site would be impossible to detect using the diffraction data employed in this analysis. Consequently, no further attempt was made to locate these oxygen atoms and the results are presented for a structural unit with composition $Mn_3[Cr(CN)_6]_2 . 12H_2O$. It is noted again, however, that since even part of the water in this unit has a typical zeolite character, there exists a rather broad range of hydration, the value at any time depending on humidity and temperature.

Cr-C and C-N distances agree well with those found in $Cd_3[Cr(CN)_6]_2 . xH_2O$,[5] where the $Cr(CN)_6$ group has the same regular octahedral symmetry. The Mn - O(1) distance is considerably longer than Mn-N. The same observation has been made in the structure of $Mn_3[Co(CN)_6]_2 . xH_2O$.[3]

Acknowledgments. We wish to tank Dr. N. W. Alcock and Dr. K. J. Watson for helpful discussions and the use of their computer programs. C, N, and H analyses were performed at the laboratories of Dr. A. Wander AG, Bern, Switzerland. The single crystal X-ray diffractometer was purchased from a grant made by Statens Naturvidenskabelige Forskningsrad (Denmark). Computations were performed on an IBM 360/75 computer at the Northern Europe University Computing Centre. The financial support of Schweiz. Nationalfonds and of the Stiftung Entwicklungsfonds Seltene Metalle is gratefully acknowledged.

---

(13) W.C. Hamilton and J.A. Ibers, *Hydrogen Bonding in Solids*, Benjamin, New York, N.Y. 1968.