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The Crystal Structure of Twinned Monoclinic Potassium Manganicyanide, $K_3[Mn(CN)_6]$

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Crystals of potassium manganicyanide were found to occur in one form only. They are monoclinic, twinned on (100) showing pseudo-orthorhombic symmetry and have the space group $P2_1/c$. The unit-cell dimensions are $a=7{\cdot}09\pm0{\cdot}009$, $b=10{\cdot}49\pm0{\cdot}007$, $c=8{\cdot}46\pm0{\cdot}006$ Å and $\beta=107{\cdot}6\pm0{\cdot}2°$; $V=599{\cdot}6\pm1$ Å^3; $\varrho_m=1{\cdot}82$ g cm^{-3}, $\varrho_{\rm calc}=1{\cdot}82$ g cm^{-3}, $Z=2$. The structure has been determined by three-dimensional X-ray analysis at 20 ± 2°C ($R=11{\cdot}93$%) and is closely isomorphous with potassium ferricyanide [Figgis, Gerloch & Mason (1969), *Proc. Roy. Soc.* A**309**, 91–118] and one monoclinic crystal form of potassium cobalticyanide [Curry & Runciman (1959), *Acta Cryst.* **12**, 674–678]. Some X-ray photographs showed that the crystals are not simply twinned, but consist of more than two individuals, and indications of lattice disorder were observed.

Introduction

Unit-cell data for potassium manganicyanide had previously been recorded in three separate X-ray investigations and the results obtained are summarized below.

a (Å)	*b* (Å)	*c* (Å)	Space group	*Z*	Reference
13·56	10·60	8·50	*Pnca*	4	Gottfried & Nagelschmidt (1930)
13·59	10·62	8·52	*Pnca*	4	Okaya *et al.* (1957)†
13·56	10·51	8·48	*Pnca*	4	Chadwick & Sharpe (1966)*

Gottfried & Nagelschmidt reported that the single crystals of potassium manganicyanide have orthorhombic symmetry. This symmetry was confirmed by Okaya *et al.*, but these authors observed indications of disorder in the single crystals similar to that which they described for potassium cobalticyanide. Chadwick & Sharpe examined powder photographs of potassium manganicyanide and noted that with the exception of three weak lines these could also be indexed on the basis of monoclinic unit cells with space group $P2_1/c$ using the relationship $a_{\rm ortho}=(2\sin\beta)a_{\rm mono}$ and $\beta=107°20'$. It might be expected that potassium manganicyanide would be isomorphous with monoclinic potassium ferricyanide and potassium cobalticyanide. However, with the exception of the suggestion of Chadwick & Sharpe mentioned above, all earlier investigations on the structure of potassium manganicyanide led to the conclusion that the symmetry is orthorhombic. In view of this anomaly an independent investigation of this structure was undertaken.

Experimental

Preparation

The blue complex potassium manganocyanide was first prepared (Christensen, 1885) and then oxidized by drawing air through the suspension of the crystals in their mother liquor to give red potassium manganicyanide. This product was recrystallized from warm water to give needle-shaped crystals, which when dry were stable in air. Although various methods of preparation and recrystallization were investigated, only one form of these crystals was obtained. The crystals varied in size and one of the largest grown had the approximate dimensions 25 × 1 × 1·5 mm. However, for X-ray photographs the dimensions of a typical needle crystal used were 1·44 × 0·09 × 0·21 mm.

Chemical analysis

Potassium was determined gravimetrically as potassium tetraphenylborate. Manganese was determined colorimetrically as potassium permanganate by measuring the optical density with a Unicam Spectrophotometer (S.P. 500). Carbon and nitrogen were determined by the combustion method. The average values from three separate determinations and the theoretical values are as follows.

	K	Mn	C	N	Total
Experimental	35·73	16·58	21·25	25·57	99·13
Theoretical	35·72	16·73	21·95	25·60	100·00

The error in all the analytical results is ±0·3% (abs).

Density

The density of crystals of various sizes was determined in a density column prepared from carbon

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† The *a* and *b* axes have been interchanged in relation to the usage of these authors, so that *a* in all cases is the longest axis.

tetrachloride and tetrabromoethane and was found to be 1·82 g cm^{-3} at 20°C.

X-ray data

Laue, oscillation and rotation photographs were taken about the three principal axes. Equi-inclination Weissenberg photographs were taken of the layers *hk*0–*hk*6, *h*0*l*–*h*3*l*, 0*kl* and 1*kl*. Cu, Cr and Co radiations were tried but the intensity values were finally obtained from the *hk*0–*hk*6 Weissenberg photographs taken with unfiltered Co radiation. All photographs were taken at 20 ± 2 °C. The relative intensities of the reflexions from the larger component of the twin on the layers where $l_M = 2n + 1$ and the superimposed reflexions for the layers where $l_M = 2n$ were measured visually and corrected for the Lorentz and polarization factors. A structure-factor diagonal least-squares refinement (Milledge, 1962) was carried out until shifts in the parameters were less than 0·25 of the standard deviations. In the calculations isotropic temperature factors were used, all reflexions were given unit weight and the cumulative error factor was found for 668 reflexions calculated with zero contribution from the unobserved reflexions, when F_{calc} was less than F_{obs} minimum.

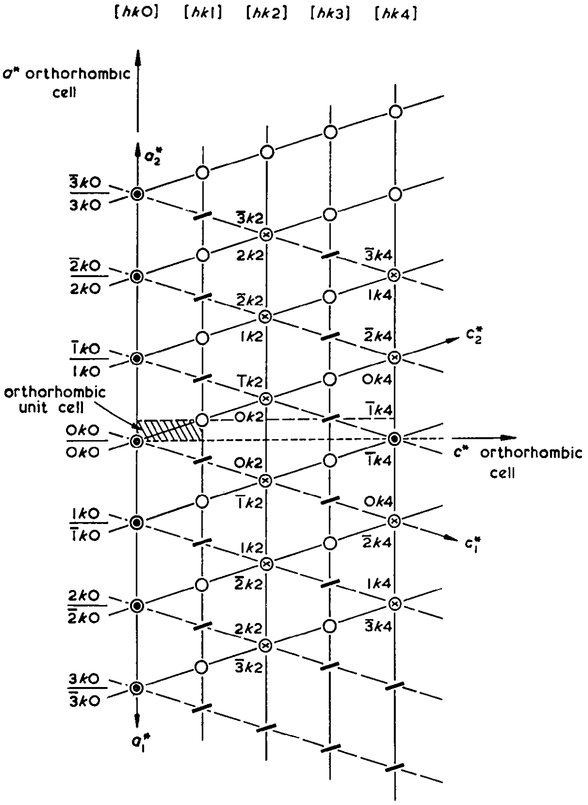

Fig. 1. Reciprocal lattice layer normal to [010] for twinned crystal of K$_3$[Mn(CN)$_5$] showing coincidences of reflexions from the two individuals of the twin (1) and (2). Encircled black dots: equivalent *hkl* coincide. Encircled asterisks: non-equivalent *hkl* coincide.

Discussion and results

The rotation photograph about the needle axis [001] gave a repeat distance of 8·46 Å but an exact horizontal mirror plane was not observed. This photograph showed that the odd layer lines of reflexions were weak in comparison with the even layer lines, indicating that the heavy atoms are probably separated by $\frac{1}{2}c$. The oscillation photograph about [010] showed a horizontal mirror plane and the repeat distance was 10·49 Å. The oscillation photograph about [100] taken at 90° to [010] also showed weak layer lines of reflexions in between lines of stronger reflexions. The spacing of the stronger layer lines corresponded to the repeat distance 13·52 Å and when the weaker layer lines of reflexions were considered $a = 27·04$ Å. The *hk*0 and *hk*1 Weissenberg photographs showed symmetry planes 90° apart. The *h*0*l* and *h*1*l* Weissenberg photographs also showed a pseudo-symmetry plane but in this case although the reflexion positions conformed to orthogonal nets the reflexion intensities showed small but definite deviations from *mm* symmetry (see below). This suggested that the true crystal symmetry could be monoclinic and that the orthorhombic arrangement of reflexion positions was due to the twin relationship of two monoclinic a^*c^* nets. The 0*kl* and the 1*kl* Weissenberg photographs again showed symmetry planes 90° apart but comparatively few reflexions were observed and no additional ones were found by increasing the exposure time. Furthermore it appeared that the direction taken as the *a* axis was not in fact a true crystallographic axis, since when the reflexions were indexed on the basis of orthorhombic symmetry no satisfactory space group could be obtained. These observations are very similar to those made by Barkatov & Zhdanov (1942) on crystals of potassium cobalticyanide which were later identified by Kohn & Townes (1961) as being of the one-layer monoclinic type, in their study of the polytypes of this complex. A new a^* axis was identified for a monoclinic unit cell on the *h*0*l* Weissenberg photograph and assuming that the crystals were twinned on (100) it was possible to describe a new unit cell with the following dimensions and estimated errors: $a = 7·09 \pm 0·009$ Å; $b = 10·49 \pm 0·007$ Å; $c = 8·46 \pm 0·006$ Å and $\beta = 107·6 \pm 0·2°$; $V = 599·6$ Å ± 1; $Z = 2$. In this monoclinic cell the *b* axis is identical with the *b* axis of the orthorhombic cell and the *c* axis is also common to both unit cells. The monoclinic *a* axis is at an angle of 107·6° to the monoclinic *c* axis, whereas the direction which was taken as the orthorhombic *a* axis is a line of pseudo-symmetry caused by the superposition of certain reflexions due to twinning. This line of pseudo-symmetry gave the appearance of an axis at 90° to the a^* axis on the *h*0*l* Weissenberg photograph. When the reflexions were indexed on the basis of a twinned monoclinic system the following conditions were found to apply: *h*0*l* is present only when $l = 2n$ and 0*k*0 is present only when $k = 2n$. This indicates that the space group is $P2_1/c$.

The new monoclinic unit cell and space group now described for potassium manganicyanide are very similar to those reported for potassium ferricyanide (Figgis, Gerloch & Mason, 1969) and potassium cobalticyanide (Curry & Runciman, 1959).

The superposition of reflexions due to twinning is illustrated in Fig. 1, from which it may be seen that where $l=2n$ there is overlapping of reflexions from both parts of the twin, but where $l=2n+1$ there is no overlap.

In general for a layer having $l=2n$, reflexions for the main crystal hkl_M and those for the twin hkl_T are superimposed when $h_M+h_T=-n$, $k_M=k_T$, and hence in particular for the zone $hk0$ and the line $1k4$ there is superposition of equivalent reflexions. It was noted that in the higher layer-line Weissenberg photographs of potassium manganicyanide where $l=2n+1$, such as $hk5$, reflexions from only one part of the twin were recorded and even these were weak. Consequently, the two parts of the twin were *unequal* but nevertheless the even layers where superposition *did* occur showed complete *mm* symmetry to the naked eye. This must indicate that the corresponding reflexions were in fact *almost* equivalent, so that whatever the relative sizes of the two twin components the even layers would appear to have *mm* symmetry. Because of this the structure factors were calculated for the layers $hk0$–$hk6$ without taking account of the contribution from the superimposed reflexions on the layers where $l_M=2n$ and these are paired for easy comparison in Table 7. The observed values are listed as though they come from the main twin.

It can be shown (*e.g.* Lonsdale, Milledge & Pant, 1965) that if I is the intensity of reflexion from the main crystal (larger individual, M) and fI is the corresponding intensity from the smaller twin (T) where f is to be determined the separate intensities could be derived as follows:

If reflexions $(h_1k_1l_1)_M$ and $(h_2k_2l_2)_T(\equiv I_1)$ are superimposed, it follows that $(h_2k_2l_2)_M$ and $(h_1k_1l_1)_T(\equiv I_2)$ are also superimposed so that when I_1 and I_2 are measured, then

$$Ih_1k_1l_1+f\,.\,Ih_2k_2l_2=I_1$$
$$f\,.\,Ih_1k_1l_1+Ih_2k_2l_2=I_2$$
$$(1-f^2)Ih_1k_1l_1=I_1-f\,.\,I_2$$

and similarly

$$(1-f^2)Ih_2k_2l_2=I_2-f\,.\,I_1\,.$$

In this case $F_{\text{calc}}(h_1k_1l_1)_T \approx F_{\text{calc}}(h_2k_2l_2)_M$ and $F_{\text{calc}}(h_2k_2l_2)_T \approx F_{\text{calc}}(h_1k_1l_1)_M$ to within about 5% for the layer lines having $l=2n$ and hence $I_M \approx I_T \pm 5\%$. f was estimated from the layer lines with $l=2n+1$ to be $\sim 0{\cdot}4$. Hence the observed intensities would never be expected to differ by more than about 15–20%, and as the intensities are estimated visually to $\pm 10\%$ it seemed unrealistic to make such a correction in this case although it is formally possible to do so. The fact that variations are in this order of magnitude is con-

Table 1. *Error factors for layers* $hk0$–$hk6$ *for* $K_3[Mn(CN)_6]$

hkl	Error factor *R*
*hk*0	10·53 %
*hk*1	9·31
*hk*2	10·56
*hk*3	11·97
*hk*4	12·26
*hk*5	13·29
*hk*6	17·46

The cumulative error factor is 11·93 %.

Table 2. *Atomic coordinates for* $K_3[Mn(CN)_6]$ *and their standard deviations*

E.s.d.'s (in parentheses) refer to last significant digits.

Atom	*x*	*y*	*z*
Mn	0 (0)	0 (0)	0 (0)
K(1)	0 (0)	0 (0)	0·5 (0)
K(2)	0·49790 (53)	0·27158 (38)	−0·12626 (50)
C(1)	0·12199 (243)	0·17301 (165)	0·02875 (229)
C(2)	0·18881 (246)	−0·05183 (166)	−0·11671 (230)
C(3)	0·19213 (243)	−0·05418 (162)	0·21642 (229)
N(1)	0·20488 (195)	0·26781 (136)	0·05368 (184)
N(2)	0·29522 (209)	−0·08484 (142)	−0·19104 (195)
N(3)	0·29851 (211)	−0·08580 (144)	0·3446 (19)

Table 3. *Isotropic temperature coefficients,* B, *for the atoms in* $K_3[Mn(CN)_6]$ *and their standard deviations (in parentheses)*

Mn	2·89 (0·07)	C(3)	2·77 (0·33)
K(1)	2·85 (0·10)	N(1)	3·02 (0·28)
K(2)	2·98 (0·07)	N(2)	3·61 (0·30)
C(1)	2·94 (0·34)	N(3)	3·80 (0·31)
C(2)	2·99 (0·34)		

Table 4. *Interatomic distances and interbond angles for* $K_3[Mn(CN)_6]$ *with their standard deviations (in parentheses)*

Inside anion

Mn—C(1)	1·990 (15) Å	C(1)–N(1)	1·140 (22) Å
Mn—C(2)	1·940 (15)	C(1)–N(2)	3·676 (23)
Mn—C(3)	2·003 (15)	C(1)–N(3)	3·746 (24)
C(1)–C(2)	2·759 (25)	C(2)–N(1)	3·635 (23)
C(1)–C(3)	2·821 (25)	C(2)–N(2)	1·157 (23)
C(2)–C(3)	2·795 (27)	C(2)–N(3)	3·744 (25)
Mn—N(1)	3·126 (15)	C(3)–N(1)	3·655 (23)
Mn—N(2)	3·096 (15)	C(3)–N(2)	3·717 (25)
Mn—N(3)	3·167 (15)	C(3)–N(3)	1·164 (25)

Outside anion

K(1)–C(3)	3·114 (15) Å
K(2)–C(1)	3·420 (18)
K(2)–N(1)	2·884 (15)
K(2)–N(2)	3·980 (15)
K(1)–N(3)	2·913 (15)

Bond angles

C(1)–Mn—C(2)	89°10′ (54′)
C(2)–Mn—C(3)	89°45′ (47′)
C(3)–Mn—C(1)	89°53′ (49′)
Mn—C(1)–N(1)	174°34′ (1°57′)
Mn—C(2)–N(2)	177°11′ (1°55′)
Mn—C(3)–N(3)	177°51′ (1°31′)

sistent with the apparent *mm* symmetry of the photographs. The error factors calculated for the layers *hk*0–*hk*6 are listed in Table 1.

The validity of the agreement obtained between the observed and calculated structure factors can be assessed by considering the *hk*0 layer separately, since the values superimposed there are equal. $R(hk0) = 10{\cdot}53\%$ and better results could not be expected for the other layer lines. For the layers with $l=2n+1$ many of the reflexions are so weak that the error factor only indicates that the agreement is reasonable. Separate refinement of these structure factors could not lead to a more reasonable result since so many of the values merely show that F_{calc} is less than F_{obs} minimum. The final observed and calculated structure factors for the three-dimensional analysis are listed in Table 7.

The final atomic coordinates in fractions of their unit-cell lengths and the isotropic temperature coefficients for the individual atoms are listed in Tables 2 and 3 respectively. The interbond distances and interbond angles are listed in Table 4, and Fig. 2 (*a*) and (*b*) shows the *hk*0 and the 0*kl* projections of the structure, respectively.

A small number of weak reflexions which could not be attributed to the two main components of the twin were observed on the *hk*1 and *hk*3 Weissenberg photographs. This indicates that the twinned crystals may consist of more than two individuals and have a lamellar structure. Then the stronger reflexions from the smaller lamellae would also appear on the photograph. The *hk*5 Weissenberg photograph was too weak for

Table 6. *Average values for metal*–C *and* C–N *distances in* $K_3[Mn(CN)_6]$ *and related complex cyanides*

Complex	M–C (Å)	C–N (Å)	M–C–N (Å)
$K_3[Mn(CN)_6]$	1·98	1·15	3·13
$K_3[Fe(CN)_6]$	1·90	1·13	3·04
$K_3[Fe(CN)_6]$(95°K)	1·94	1·13	3·07
$H_4[Fe(CN)_6]$	1·89	1·15	3·04
$K_3[Co(CN)_6]$	1·89	1·15	3·04

Table 5. *Comparison of the unit cells of* $K_3[Mn(CN)_6]$ *with those of related complex cyanides*

Formula	Symmetry	Space group	*a*	*b*	*c*	*β*	*V*	*Z*
$K_3[Mn(CN)_6]$	Monoclinic	$P2_1/c$	7·09 Å	10·49 Å	8·46 Å	107°38′	600 Å³	1
$K_3[Fe(CN)_6]$	Monoclinic	$P2_1/c$	7·06	10·38	8·40	107°0′	589	2
$K_3[Fe(CN)_6]$(95°K)	Monoclinic	$P2_1/c$	7·03	10·31	8·35	107°12′	579	2
$H_4[Fe(CN)_6]$	Monoclinic	$P2_1/c$	6·94	11·34	6·13	105°15′	465	2
$K_3[Co(CN)_6]$	Monoclinic	$P2_1/c$	7·10	10·40	8·40	107°20′	592	2
$K_4[Fe(CN)_6].3H_2O$	Monoclinic	$C2/c$	9·32	16·84	9·32	90°0′	1462	4

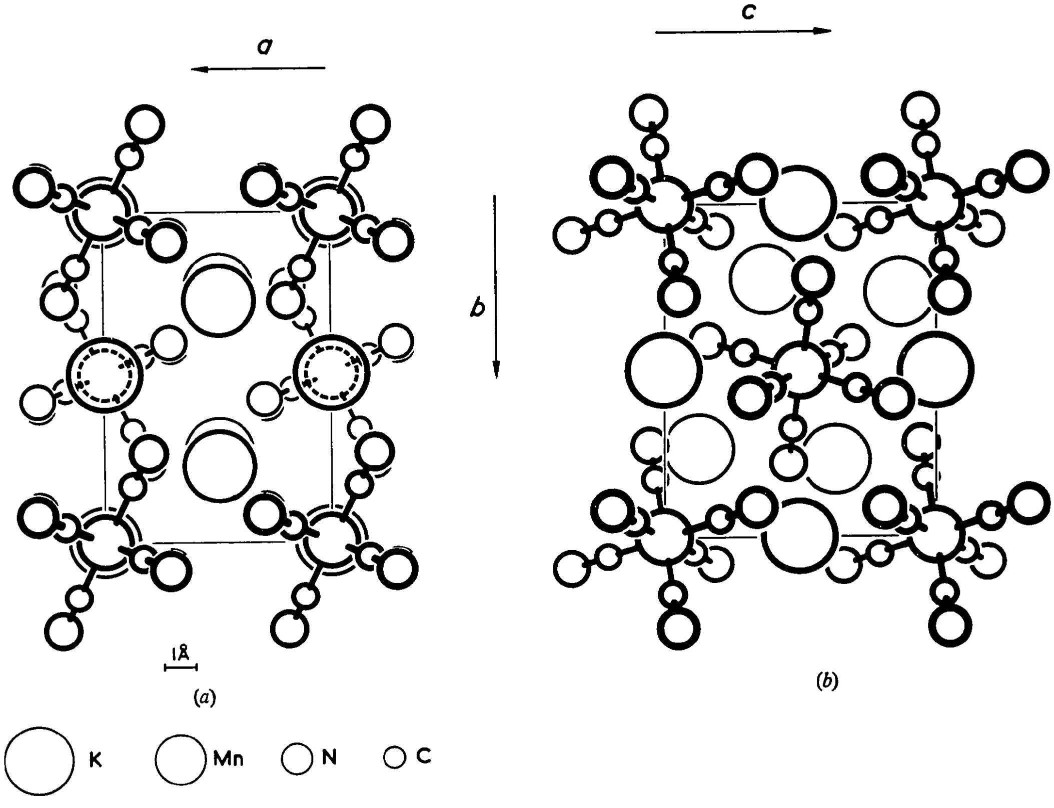

Fig. 2. (*a*) *hk*0 projection of the crystal structure $K_3[Mn(CN)_6]$. (*b*) 0*kl* projection of the crystal structure $K_3[Mn(CN)_6]$.

Table 7. $|F_{obs}|$ *and* F_{calc} *for* $K_3[Mn(CN)_6]$

H	K	L	F(OBS)	F(CALC)
1	0	0•	8.07	9.01
2	0	0•	12.18	12.27
3	0	0•	4.29	-1.64
4	0	0•	17.25	19.86
5	0	0•	2.48	1.54
6	0	0•	10.11	12.08
7	0	0•	1.86	0.94
0	2	0•	9.50	8.53
0	4	0•	25.68	25.02
0	6	0•	2.04	-2.09
0	8	0•	6.89	6.91
0	10	0•	4.10	2.91
1	1	0•	1.02	-0.11
2	1	0•	7.93	-6.78
3	1	0•	3.07	-2.91
4	1	0•	3.76	3.46
5	1	0•	2.50	0.01
6	1	0•	2.77	-0.47
7	1	0•	1.89	0.67
1	2	0•	34.14	30.31
2	2	0•	2.59	-0.89
3	2	0•	23.19	24.40
4	2	0•	3.18	3.29
5	2	0•	10.04	12.79
6	2	0•	2.71	2.19
7	2	0•	7.23	7.46
1	3	0•	18.46	20.00
2	3	0•	1.62	1.29
3	3	0•	6.59	-6.62
4	3	0•	2.35	-1.17
5	3	0•	2.50	0.14
6	3	0•	2.60	-0.11
7	3	0•	1.86	2.08
1	4	0•	5.85	6.24
2	4	0•	21.29	20.74
3	4	0•	2.09	-0.93
4	4	0•	14.87	14.75
5	4	0•	4.85	5.33
6	4	0•	8.21	8.42
7	4	0•	1.52	-0.42
1	5	0•	6.30	5.77
2	5	0•	2.03	2.04
3	5	0•	2.32	-0.68
4	5	0•	2.50	0.21
5	5	0•	2.82	-1.39
6	5	0•	2.15	-0.56
1	6	0•	15.61	17.89
2	6	0•	9.18	10.27
3	6	0•	11.40	11.42
4	6	0•	2.50	0.21
5	6	0•	8.83	7.79
6	6	0•	1.71	0.87
1	7	0•	2.39	0.42
2	7	0•	2.46	1.69
3	7	0•	2.50	-1.21
4	7	0•	2.68	-3.61
5	7	0•	2.26	0.29
1	8	0•	3.50	3.60
2	8	0•	10.32	10.95
3	8	0•	5.82	4.46
4	8	0•	8.39	7.25
5	8	0•	2.47	2.61
1	9	0•	2.86	-2.31
2	9	0•	2.75	1.43
3	9	0•	3.00	1.55
4	9	0•	1.92	-1.09
1	10	0•	6.25	4.63
2	10	0•	4.96	4.38
3	10	0•	7.65	7.02
0	1	1	6.91	7.07
1	1	1	6.19	6.64
2	1	1	2.30	-0.67
3	1	1	3.00	0.11
4	1	1	3.56	0.78
5	1	1	3.83	2.60
6	1	1	3.93	0.52
0	2	1	3.02	-2.67
1	2	1	3.22	2.79
2	2	1	3.55	-3.09
3	2	1	3.10	-0.67
4	2	1	3.63	-3.01
5	2	1	3.81	2.22
6	2	1	3.83	0.80
0	3	1	6.04	6.34
1	3	1	2.83	-2.67
2	3	1	2.67	3.13
3	3	1	3.26	0.14
4	3	1	6.33	5.53
5	3	1	3.76	1.36
6	3	1	3.61	1.74
0	4	1	5.41	4.83
1	4	1	2.69	-1.25
2	4	1	7.85	6.94
3	4	1	3.46	-2.17
4	4	1	3.80	1.29
5	4	1	5.17	-2.66
6	4	1	3.30	1.13
0	5	1	2.91	-1.67
1	5	1	6.83	7.00
2	5	1	3.34	-0.56
3	5	1	5.79	4.76
4	5	1	3.82	-2.68
5	5	1	4.08	1.35
6	5	1	2.79	-0.45
0	6	1	3.31	-3.50
1	6	1	8.25	7.10
2	6	1	3.49	-3.26
3	6	1	3.81	1.35
4	6	1	5.20	-4.08
5	6	1	3.68	2.62
0	7	1	5.11	6.69
1	7	1	3.71	-2.40
2	7	1	4.58	4.36
3	7	1	3.79	-1.73
4	7	1	4.05	3.12
5	7	1	3.04	-1.47
0	8	1	3.82	3.43
1	8	1	3.68	-4.68
2	8	1	3.78	2.45
3	8	1	4.16	-2.91
4	8	1	3.46	2.92
0	9	1	3.56	-5.36
1	9	1	4.29	3.46
2	9	1	4.04	-0.04
3	9	1	4.06	4.59
4	9	1	2.50	-1.52
0	10	1	3.80	-2.40
1	10	1	3.65	4.23
2	10	1	3.25	-1.73
3	10	1	2.46	2.26
1	11	1	2.53	-1.28
-1	1	1	8.56	8.97
-2	1	1	1.70	0.90
-3	1	1	2.25	0.21
-4	1	1	2.79	-0.45
-5	1	1	3.25	2.67
-6	1	1	3.80	1.26
-1	2	1	2.49	-2.65
-2	2	1	2.61	2.47
-3	2	1	4.69	-3.85
-4	2	1	2.89	-0.85
-5	2	1	3.29	-1.29
-6	2	1	3.74	2.30
-1	3	1	2.15	-2.13
-2	3	1	3.31	3.39
-3	3	1	2.44	-1.51
-4	3	1	6.37	5.50
-5	3	1	3.32	1.78
-6	3	1	3.50	3.17
-1	4	1	4.79	6.07
-2	4	1	2.39	-0.14
-3	4	1	5.53	5.17
-4	4	1	3.16	-2.87
-5	4	1	3.32	0.60
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5	1	3	3.46	-1.37
6	1	3	2.68	1.90
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2	3	3	2.86	1.75
3	3	3	5.46	5.13
4	3	3	3.82	-0.11
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5	5	3	2.54	-1.16
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2	6	3	3.27	-2.96
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-3	8	6	4.61	3.25]
1	8	6	4.31	4.25]
-4	8	6	4.52	4.30]
-1	0	6	7.92	11.67
-5	0	6	2.96	1.60
-1	1	6	4.39	-4.36
-5	1	6	5.46	-4.57
-1	2	6	5.61	7.11]
-2	2	6	4.86	6.69]
-1	3	6	4.82	5.19]
-2	3	6	4.82	5.37]
-1	4	6	6.64	8.26]
-2	4	6	7.50	8.93]
-1	5	6	3.69	-4.12]
-2	5	6	4.36	4.14]
-1	6	6	6.27	6.02]
-2	6	6	6.36	5.89]
-1	7	6	3.20	0.60]
-2	7	6	2.93	-1.10]

EXPLANATION OF SYMBOLS USED

• = REFLEXIONS FOR WHICH DATA FOR BOTH TWINS IS SUPERPOSED

OBSERVED VALUES THEREFORE MULTIPLIED BY APPROPRIATE SCALE FACTOR FOR RELATIVE SIZES FOR THE TWIN COMPONENTS

] = REFLEXIONS FOR WHICH DATA FOR BOTH COMPONENTS OF THE TWIN ARE SUPERPOSED

VALUES FOR ALL OTHER REFLEXIONS OBTAINED FROM DATA FROM THE LARGER TWIN COMPONENT this effect to be observed. Also, streaks were observed on the *hk*1 and *hk*3 Weissenberg photographs parallel to **a*** at integral and non-integral *k*. This could indicate one-dimensional disorder in the direction parallel to (100) and resembles that described by Okaya *et al.* (1957) in their study of potassium cobalticyanide and the corresponding salts of chromium iron and manganese.

It may be seen from Table 5 that the unit-cell dimensions and space group of potassium manganicyanide are very similar to those of the related complex cyanides which have been studied, with the exception of the hydrated potassium ferrocyanide (Pospyelov & Zhdanov, 1947).

The atomic positions of potassium manganicyanide and the corresponding salts of iron (Figgis, Gerloch & Mason, 1969) and cobalt (Curry & Runciman, 1959) are all similar and the metal–ligand interatomic distances in these complexes and in hydrogen hexacyanoferrate(II) show a close resemblance to one another. Although due account must be taken of errors in the structures and hence in bond lengths some general trends involving bond lengths in these related compounds may be observed.

In Table 6 it may be seen that metal–carbon bond distances tend to decrease slightly with increasing nuclear charge of the metal ion and the corresponding carbon-to-nitrogen interatomic distances generally tend to increase. These values are consistent with the expected charge distribution along the metal –C–N bond. Also, these metal –C–N bonds appear to be linear and their lengths tend to decrease in the manner predicted by Chadwick & Sharpe (1966) who found that the volumes of the unit cells decreased in the order potassium manganicyanide > potassium ferricyanide > potassium cobalticyanide and stated that provided the octahedra in these complexes are not severely distorted the metal–ligand distances should be reflected in the molecular volumes.

In conclusion it may be said that although the cumulative error factor for potassium manganicyanide was found to be 11·93 %, thus indicating that the structure described is generally correct, there are a number of factors which influence the accuracy of the data listed and the introduction of further corrections could lead to an adjustment of atomic positions and bond lengths. In the layer-line Weissenberg photographs *hk*0–*hk*6 of the monoclinic potassium manganicyanide, the layer lines where $l_M = 2n+1$ should have been particularly valuable for assessing the error factors, because here the lattices of the monoclinic individuals were separated. However, these photographs gave mainly weak reflexions and the intensity measurements and resulting error factors could not be considered to be very reliable. On the layer-line Weissenberg photographs where $l_M = 2n$ the superimposed reflexions were not separated before carrying out the least-squares refinement. Consequently, it is possible that differences between F_{obs} and F_{calc} values in these layers could be reduced by determining the relative contributions from the monoclinic individuals of the twin and recalculating the structure factor. Also, isotropic temperature factors were used and although the introduction of anisotropic temperature factors into the structure-factor calculations would result in lower error factors this improvement would be spurious unless the data were first untwinned. However, because of the nature of potassium manganicyanide and the presence of disorder and lamellae in the structure, it was considered that a more rigorous treatment of the crystallographic data would not yield a significantly more accurate result.

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