The Crystal Structure of Cadmium (II) Hexacyano-chromate (III), $Cd_3[Cr(CN)_6]_2 \cdot xH_2O$

HANS U. GÜDEL*

Kemisk Laboratorium IV, H. C. Ørsted Institutet, Universitetsparken 5, DK-2100 København Ø, Danmark

The crystal structure of $Cd_3[Cr(CN)_6]_2 \cdot xH_2O$ has been determined from three-dimensional X-ray diffraction data measured by counter methods. The cubic face-centred unit cell with space group $O^3 - F432$, $T_d{}^2 - F\bar{4}3m$, or $O_h{}^5 - Fm3m$ has $a = 10.899(4)$ Å and contains 1 ⅓ formula units. The structure was determined by comparison with, and subsequent modification of, the known structural model for hexacyanocobaltate(III) compounds. Least squares refinement of the positional parameters and individual atomic isotropic temperature factors for a statistically disordered structure led to a final R value for the observed reflections of 0.035.

The crystal structure is very closely related to the structures of other Prussian Blue analogue compounds. Cadmium 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 cadmium atom has a mixed coordination, its averaged composition being CdN_4O_2. All cyanide groups are bridged between chromium and cadmium atoms, with the carbon atoms bonded to chromium. The $Cr-C$, $C-N$, $Cd-N$, and $Cd-O(1)$ distances are 2.05(2), 1.14(3), 2.27(2), and 2.39(4) Å, respectively.

T he crystal structure of $Cd_3[Cr(CN)_6]_2 \cdot xH_2O$ has been described in terms of a model developed for Prussian Blue by Keggin and Miles [1,2] in 1936. Recently the validity of this model has been questioned, preparative, spectroscopic, and X-ray diffraction studies on a series of Prussian Blue analogue hexacyanocobaltate(III) compounds leading to the postulate of a new structural model.[3-5] Since most of the polynuclear Prussian Blue analogue cyanides give a simple X-ray diffraction powder pattern corresponding to a cubic face-

centred unit cell with a lattice constant of about 10 Å,[6] it seems reasonable to assume that their crystal structures are closely related. It was therefore one of the purposes of the present investigation to determine if our structural model developed for the hexacyanocobaltate(III) compounds can also be applied to the hexacyanochromate(III) analogues. Moreover, this is to our knowledge the first crystal structure analysis of a compound containing the group $Cr(CN)_6^{3-}$; it was therefore anticipated that accurate interatomic distances could be obtained and that, in particular, comparisons of the $Cr-C$ distances could be made with those of $Co-C$ in $Co(CN)_6^{3-}$ and $Fe-C$ in $Fe(CN)_6^{3-}$.

EXPERIMENTAL

Single crystals of $Cd_3[Cr(CN)_6]_2.xH_2O$ were prepared by Dr. A. Ludi and Dr. G. Ron at the Institut für anorganische, analytische und physikalische Chemie of the University of Bern, Switzerland, using a procedure which has been described previously.[5] In this case the two inter-diffusing components were cadmium(II) chloride and potassium hexacyanochromate(III).

Analysis. Carbon, nitrogen, and hydrogen analyses were performed at the analytical laboratory of Dr. A. Wander AG, Bern. A thermogravimetric analysis for water was also made. Results: Calculated for $Cd_3[Cr(CN)_6]_2.12H_2O$: C 14.9; N 17.3; H 2.5; H_2O 22.3. Calculated for $Cd_3[Cr(CN)_6]_2.14H_2O$: C 14.3; N 16.7; H 2.8; H_2O 24.3. Found: C 14.2; N 15.9; H 2.8; H_2O 26.5. The water content is sensitive to changes of humidity and temperature so that, near room temperature, x lies in the range $12 < x < 15$.

Unit cell. X-Ray diffraction powder photographs taken on a Guinier camera using $FeK\alpha$ radiation, and Weissenberg single crystal photographs taken with $MoK\alpha$ radiation showed that $Cd_3[Cr(CN)_6]_2.xH_2O$ has a cubic face-centred unit cell with axial length approximately 10.9 Å. A cube-shaped crystal with an edge length of 0.063 mm was later mounted on a Picker FACS-1 single crystal X-ray diffractometer with a graphite-monochromated $MoK\alpha$ 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: $a = 10.899(4)$ Å, where the figure in parenthesis is the estimated standard deviation.

Density. The density of the single crystals was measured both pycnometrically (decahydronaphthalene) and by flotation (chlorobenzene-methyl iodide). Corresponding densities were calculated assuming that, as in the hexacyanocobaltate(III) analogues, there were $1\frac{1}{3}$ formula units in the unit cell. This assumption was shown to be correct in the subsequent structure analysis. Results: D (calc. for $x=12$), 1.66 g/cm³. D (calc. for $x=14$), 1.72 g/cm³. D (measured), 1.70(5) g/cm³, where the figure in parenthesis is the estimated error. These are in agreement with the analysis figures, again indicating that the water content is somewhat higher than 12 molecules per formula unit.

Measurement and reduction of diffraction data. The same crystal as that used for the unit cell determination was mounted. Diffracted intensities in one octant of the reciprocal lattice were measured using $MoK\alpha$ radiation and the moving crystal-moving counter (2θ-scan) technique. The counter scan range was 2.2 degrees at $2\theta = 0°$, and was increased automatically with increasing 2θ to allow for dispersion. The scan rate was 1°/min. Background counts for 10.00 sec each were made at both ends of the 2θ-scan range. 615 reflections, of which 144 were independent, were sampled in the range $0.092 \leq \sin\theta/\lambda \leq 0.734$. The data for each reflection were checked for reasonable background counts and for other indications of possible machine malfunctions, were converted to net counts (scan count minus time-corrected background count) and then were corrected for Lorentz and polarization effects with a version of the NRC-2A programme[9] which has been extensively modified for local use by Dr. N. W. Alcock. Absorption corrections were then applied using the ABSCOR programme.[10,11] The minimum and maximum transmission factors were 0.852 and 0.893, respectively. Since the computer programmes to be used later for Fourier summations required an independent set of data, equivalent reflections were averaged. Averaged reflections were designated as "unobserved" when the ratio $\sigma(|F|)/|F|$, where $\sigma(|\bar{F}|)$ is the estimated standard deviation of structure amplitude

$|F|$, was greater than 6, this condition being very close to the condition $\sigma(I)/I$ greater than 3 for the individual measured intensities, I. Thus an independent set of 90 observed and 54 unobserved reflections was obtained.

Space group. As expected from the X-ray diffraction powder patterns, Weissenberg photographs exhibited the absences $h+k$, $h+l$, $k+l \neq 2n$, corresponding to a cubic face-centred unit cell. No further systematic extinctions could be 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 $hk0$ and $kh0$, and also hkl and hlk had the same corrected intensities. The space groups with Laue group $T_h - m3$ could thus be excluded.[12] However, no discrimination between the three remaining possible space groups could be made.

ANALYSIS AND DESCRIPTION OF THE STRUCTURE

The structural model developed for hexacyanocobaltate(III) compounds was used as a starting point for this analysis. Accordingly 4 cadmium atoms were placed at the positions $4a$ (0,0,0), 4 chromium atoms with occupation factors 2/3 were placed at positions $4b$ (0.5, 0.5, 0.5), and 24 carbon atoms and 24 nitrogen atoms, also with occupation factors 2/3, were assigned to the 24-fold positions $(x,0,0)$. x_C and x_N were chosen such that the Cd $-$ N and N $-$ C distances were 2.25 Å and 1.15 Å, respectively, in analogy with the corresponding distances determined previously for $Cd_3[Co(CN)_6]_2 \cdot xH_2O$.[3]

In each of the possible space groups the positions that were assumed for the Cd, Cr, N, and C atoms have the same respective multiplicities. Therefore, structure factors only including these atoms (individual atomic isotropic temperature factors were also postulated by analogy) and a difference electron density map was computed. The map showed two independent, broad, positive regions centred at (0.22,0,0) and (0.25,0.25,0.25). Oxygen atoms (O(1) and O(2)) were postulated at general positions near to these sites. In space group $T_d^2 - F\bar{4}3m$, where the positions (0.25,0.25,0.25) and (0.75,0.75,0.75) are not equivalent, oxygen atoms O(2) were placed near to either of the two positions. General equivalent positions have multiplicities of 192 in $O_h^5 - Fm3m$, and 96 in $O^3 - F432$ and $T_d^2 - F\bar{4}3m$. Hence it was assumed that the oxygen atoms are statistically distributed, each general position being occupied, on average, by 1/12 $(T_d^2 - F\bar{4}3m$ (O(1)) and $O^3 - F432)$ or 1/24 $(T_d^2 - F\bar{4}3m$ (O(2)) and $O_h^5 - Fm3m)$ of an oxygen atom.

The structural parameters were refined using a full matrix least squares procedure. The function minimized was $\sum w(||F_{obs}| - |F_{calc}||)^2$, where the summation was 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.,[13] 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 Cd^{2+}, Cr, C, $N^{0.5-}$, and O, tabulated by Ibers.[14] Since Cd^{2+} was not tabulated the corresponding values for Ag^+ were taken, and 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.[21] Corrections for the real part, $\Delta f'$, of the anomalous scattering were applied where appropriate.[14] 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. Refinements were carried out in all three possible space groups.

The final reliability factors are $R = 0.035$ and $R_w = 0.041$ in $O_h^5 - Fm3m$ and $O^3 - F432$, and $R = 0.033$ and $R_w = 0.038$ in $T_d^2 - F\bar{4}3m$, where the normal reliability factor is defined as $R = \sum ||F_{obs}| - |F_{calc}||/\sum |F_{obs}|$ and the weighted reliability factor is $R_w = (\sum w(|F_{obs}| - |F_{calc}|)^2/\sum wF_{obs}^2)^{\frac{1}{2}}$ the summation being taken over all observed reflections.

All the computations described in this section were performed using the XRAY System programmes of Stewart et al.[15]

The results show that the crystal structure of $Cd_3[Cr(CN)_6]_2.xH_2O$ can be described equally well in either space group, $T_d^2 - F\bar{4}3m$, $O^3 - F432$, or $O_h^5 - Fm3m$. That the reliability factors from the refinement in $T_d^2 - F\bar{4}3m$ are slightly lower than those from the refinements in the two other space groups is to be expected, since the oxygen atoms O(2) occupy two independent general positions, and thus the number of parameters describing the calculated structure is increased by four. All final parameters of the two refinements in $O^3 - F432$ and $O_h^5 - Fm3m$ differ by less than one estimated standard deviation. That both refinements should have led to equally good agreement between calculated and observed structure amplitudes is understandable since both O(1) and O(2) occupy sites very close to the special position (x,x,y) (Table 1), and this has the same multiplicity in both $O^3 - F432$ and $O_h^5 - Fm3m$. The final parameters of the oxygen atoms O(2) obtained from the refinement in $T_d^2 - F\bar{4}3m$ differ by one to three estimated standard deviations from those of the refinement in $O_h^5 - Fm3m$; all the other parameters differ by less than one standard deviation. If, therefore, the crystal structure of $Cd_3[Cr(CN)_6]_2.xH_2O$ is non-centrosymmetric, the deviation from centrosymmetry is very small. For simplicity only the results of the refinement in space group $O_h^5 - Fm3m$ are given in Tables 1 to 3.

A further refinement of the structure was performed with the oxygen atoms O(1) and O(2) restricted to the positions $24e$ $(x,0,0)$ and $8c$ $(0.25,0.25,0.25)$, respectively. With final reliability factors $R = 0.046$ and $R_w = 0.056$ and temperature factors of 18.6 Å^2 and 26.0 Å^2 for O(1) and O(2), respectively, this possibility proved to be unrealistic and was excluded. The shortest $O(1) - O(2)$ interatomic distance would be 3.87 Å in this case, a distance that is considerably longer than corresponding distances in hydrogen bonded systems.[16] Thus, if we assume that the oxygen atoms O(2) are bonded by hydrogen bridges to the atoms O(1), it is quite understandable that the equilibrium positions of both of them are close to but not at the special positions $24e$ and $8c$.

Table 1. Final structural parameters of $Cd_3[Cr(CN)_6]_2 \cdot xH_2O$ 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.

|		
Cd	B	3.42(6)
Cr	B	2.66(13)
C	x/a	0.3121(18)
	B	3.86(35)
N	x/a	0.2078(17)
	B	5.10(37)
O(1)	x/a	0.2133(38)
	y/b	0.0376(54)
	z/c	0.0323(58)
	B	4.19(112)
O(2)	x/a	0.1983(75)
	y/b	0.2235(76)
	z/c	0.2828(74)
	B	11.29(268)

Table 2. Observed structure amplitudes, $|F_{obs}|$, and calculated structure factors, F_{calc} (in electrons $\times 10$). 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, $10|F_{obs}|$, $10F_{calc}$.

0,0,L

l	$10|F_{obs}|$	$10F_{calc}$
2	2651	2717
4	3148	3211
6	1996	1938
8	1092	1099
10	878	879
12	446	458
14	352	317
16	277	190

0,2,L

2	2096	2037
4	1907	1846
6	1419	1436
8	838	862
10	738	718
12	399	396
14	280	275

0,4,L

4	2087	2028
6	1323	1404
8	811	843
10	705	691
12	371	381
14	269	260

0,6,L

6	1083	1090
8	669	707
10	562	578
12	325	342
14	253	228

0,8,L

8	481	470
10	404	399

0,0,L (cont.)

12	224*	246

0,10,L

10	331	327
12	194*	209

1,1,L

1	1234	1220
3	1111	968
5	954	911
7	439	449
9	476	456
13	147*	164
15	87*	88

1,3,L

3	690	768
5	810	796
7	464	426
9	443	442
11	207*	207
13	179*	172
15	122*	95

1,5,L

5	628	631
7	379	384
9	332	330
11	138*	150
13	133*	124
15	104*	65

1,7,L

7	263	278
9	249	257
11	140*	136

1,1,L (cont.)

13	116*	112

1,9,L

9	214*	198
11	105*	108
13	74*	84

1,11,L

11	77*	62

2,2,L

2	278	310
4	1288	1272
6	964	949
8	626	606
10	610	597
12	338	322
14	257*	235

2,4,L

4	1300	1317
6	1058	1040
8	658	649
10	587	561
12	335	317
14	263	221

2,6,L

6	816	840
8	541	542
10	492	475
12	290	281
14	172*	192

2,8,L

8	351	357

2,2,L (cont.)

10	353	319
12	213*	196

2,10,L

10	288	267
12	135*	170

3,3,L

3	852	742
5	690	643
7	390	443
9	426	416
11	206*	217
13	162*	176
15	125*	98

3,5,L

5	584	607
7	356	350
9	326	329
11	166*	157
13	155*	129

3,7,L

7	290	287
9	248	248
11	134*	138
13	134*	112

3,9,L

9	205*	197
11	108*	109

3,11,L

11	103*	62

4,4,L

4	1313	1393
6	1035	1047
8	645	651
10	927	547
12	299	312
14	225*	213

4,6,L

6	789	836
8	538	551
10	454	462
12	267	278
14	186*	187

4,8,L

8	361	368
10	329	320
12	204*	198

4,10,L

10	260*	267

5,5,L

5	433	435
7	272	314
9	249	248
11	118*	121
13	140*	98

5,7,L

7	209*	220
9	189*	200
11	156*	104
13	147*	86

5,9,L

9	179*	159
11	112*	87

6,6,L

6	470	690
8	441	464
10	385	393
12	218*	242

6,8,L

8	312	316
10	262	275
12	179*	172

6,10,L

10	211*	230

7,7,L

7	234*	181
9	177*	154
11	134*	84

7,9,L

9	101*	128
11	110*	70

8,8,L

8	187*	215
10	150*	193

9,9,L

9	176*	107

Table 3. Some interatomic distances (Å) in $Cd_3[Cr(CN)_6]_2 \cdot xH_2O$. The figures are those from the refinement in space group $O_h^5 - Fm3m$. Only the four shortest $O(1) - O(2)$ distances are given. Estimated standard deviations ($\times 10^3$) are given in parentheses.

Cd $-$ N	2.265(19)
Cr $-$ C	2.047(19)
C $-$ N	1.137(27)
Cd $-$ O(1)	2.386(43)
O(1) $-$ O(2)	2.754(101)
	2.819(100)
	2.825(101)
	3.016(100)

Cadmium atoms occupy the sites 4a (0,0,0) of the cubic face-centred unit cell. Two thirds of the sites 4b (0.5,0.5,0.5) are occupied by chromium atoms and the corresponding two thirds of two sets of the sites 24e, (0.312,0,0) and (0.209,0,0), are occupied by carbon and nitrogen atoms, respectively. Oxygen atoms are situated near to the vacant sites left by the nitrogen atoms (O(1)) and near to the positions 8c (0.25,0.25,0.25) (O(2)), each atom of this latter type occupying one of the eight small cubes (Fig. 1) of the unit cell.
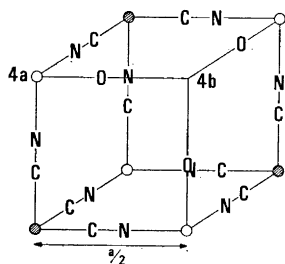
Fig. 1. Schematic diagram of one eighth of a unit cell of $Cd_3[Cr(CN)_6]_2 \cdot xH_2O$ illustrating the mixed coordination of nitrogen and oxygen around the cadmium atoms. O and ● designate Cd and Cr atoms, respectively. The $Cr(CN)_6$ unit centred at the corner 4b of the small cube is supposed to be absent.

DISCUSSION

The coordination units centred at the positions 4b may be assumed to be $Cr(CN)_6$ octahedra with the incomplete occupancy arising from the absence of whole units in a completely random manner. The $Cr(CN)_6$ ions are, by symmetry, perfectly regular octahedra. The cadmium atoms have a mixed nitrogen and oxygen (O(1)) coordination of the average composition CdN_4O_2. Thus, although both positions 4a and 4b have site symmetry $m3m$,[14] the actual microsymmetry at the points occupied by the cadmium atoms is lower due to the statistical absence of one third of the $Cr(CN)_6$ units. Fig. 1 shows an illustration of the mixed coordination around the cadmium atoms. It can also be seen from this diagram that all cyanide groups act as bridges between chromium and cadmium atoms, with the carbon atoms always directed towards the chromium atoms.

While the oxygen atoms O(1) form part of the coordination unit of cadmium, the atoms O(2) are relatively free, probably being attached by hydrogen bonds to the coordinated atoms O(1). The O(1) − O(2) interatomic distances (Table 3) agree well with oxygen-oxygen distances in other systems that do form such hydrogen bonds.[16] 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 analogue compounds,[3,5] 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.

Chemical analysis and the measured density indicate that the number of water molecules is 13 or 14, rather than 12 as assumed in this crystal structure determination. 5 cycles of least squares refinement moving only the population parameters of the oxygens led to populations of 0.99 and 1.01 for O(1) and O(2), respectively, with the same reliability factors, thus indicating that the occupancies originally assumed for O(1) and O(2) are right. 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 2 % 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 any one 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 $Cd_3[Cr(CN)_6]_2.12H_2O$. 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 upon humidity and temperature.

This crystal structure is very closely related to the structures found in Prussian Blue analogue hexacyanocobaltate(III) compounds. Thus the statistical disorder with random absence of the groups $M^A(CN)_6$, and the participation of the oxygen atom of a water molecule in the coordination of metal atom B is the same. The assumption that many other members of the large Prussian Blue family have a similar crystal structure would seem to be justified.

The Cr − C distance in $Cd_3[Cr(CN)_6]_2.12H_2O$ is 2.05 Å. This may be compared with Co − C distances between 1.87 Å and 1.89 Å in compounds containing the group $Co(CN)_6^{3-}$[5,7,17,18] and with Fe − C distances between 1.89 Å and 1.92 Å in $K_3Fe(CN)_6$.[19] As has already been predicted from the unit cell dimensions of the series of salts $K_3M(CN)_6$, $M = Cr^{3+}$, Mn^{3+}, Fe^{3+}, Co^{3+}, there is a steady decrease in the size of these ions in octahedral low spin complexes. The length of Mn − C in $Mn(CN)_6^{3+}$ may therefore be estimated to be about 1.99 Å.

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