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X-ray Powder Diffraction Data for $Cd_3[Cr(CN)_6]_2 \cdot 14H_2O$

W. O. MILLIGAN and D. F. MULLICA

Department of Chemistry and Physics, Baylor University, Waco, Tex. 76703, U.S.A.

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Introduction

X-ray powder patterns of the $A_3^{II}[B^{III}(CN)_6]_2 \cdot xH_2O$ type system yield a cubic face-centered unit cell with lattice constants of approximately 10.5 Å [1]. An indefinite amount of water of crystallization has often been associated with some of the compounds of the isostructural series. Such is the case with $Cd_3[Cr(CN)_6]_2 \cdot xH_2O$ [2]. This paper is part of a series of research studies on zeolitic properties of hydrated lanthanide and transition metal complexes of cyanides so that weak aspects in the theories of semi-permeable membranes can be partially resolved.

Experimental

Clear cube-shaped single crystals of the title compound were prepared by the U-tube slow diffusion method. Very dilute solutions of cadmium(II) chloride and potassium hexacyanochromate(III), both ACS grade, were the interdiffusing constituents. Synthesis and preliminary analyses were carried out at 290 K and at a relative humidity of 52–55%. The observed experimental density (Flotation) measured 1.70(1) Mg m^{-3} and a thermogravimetric analysis yielded 13.9(2) water molecules per formula unit.

The X-ray powder diffraction data reported here for $Cd_3[Cr(CN)_6]_2 \cdot 14H_2O$ were obtained in an evacuated 114.8 mm diameter Siemens cylindrical camera at 290 K, using nickel-filtered copper K_α radiation (mean λ = 1.54184 Å). Crystals were finely ground and placed into small diameter (0.2 mm) thin-walled glass capillaries. The observed and calculated spacing (in Å) and the visual estimated relative intensities based on 100 as the intensity for the strongest observed reflection are given in Table I. Measured 2θ values were placed into a least-squares program designed for structural powder X-ray data by Roof [3]. This computer program employs the

TABLE I. X-ray Powder Diffraction Data for $Cd_3[Cr(CN)_6]_2 \cdot 14H_2O$.

h k l	$2\theta_o$	$2\theta_c$	I/I_o	d_o	F_N[a]
1 1 1	14.000	13.9943	80	6.326	175(0.0057,1)
2 0 0	16.200	16.1728	100	5.471	61(0.0165,2)
2 2 0	22.924	22.9490	90	3.879	52(0.0193,3)
3 1 1	26.925	26.9791	80	3.311	36(0.0280,4)
2 2 2	28.175	28.2030	10	3.167	36(0.0280,5)
4 0 0	32.650	32.6794	95	2.7426	35(0.0282,6)
3 3 1	35.724	35.7058	10	2.5134	37(0.0268,7)
4 2 0	36.650	36.6659	90	2.4520	39(0.0254,8)
4 2 2	40.300	40.3098	60	2.2379	42(0.0237,9)
5 1 1	42.850	42.8717	60	2.1105	43(0.0235,10)
4 4 0	46.876	46.8893	60	1.9382	44(0.0226,11)
5 3 1	49.200	49.1766	40	1.8519	44(0.0226,12)
6 0 0	49.925	49.9215	70	1.8267	47(0.0212,13)
6 2 0	52.824	52.8242	55	1.7331	50(0.0199,14)
5 3 3	54.950	54.9309	5	1.6710	51(0.0196,15)
6 2 2	55.625	55.6205	25	1.6523	53(0.0187,16)
4 4 4	58.300	58.3234	20	1.5827	53(0.0190,17)
5 5 1	60.325	60.3036	5	1.5343	52(0.0191,18)
6 4 0	60,925	60.9521	30	1.5306	51(0.0195,19)
6 4 2	63.475	63.4785	30	1.4655	53(0.0187,20)
7 3 1	65.375	65.3996	10	1.4275	53(0.0190,21)
8 0 0	68.500	68.4804	10	1.3698	53(0.0190,22)
8 2 0	70.900	70.8993	30	1.3292	53(0.0182,24)
8 2 2	73.275	73.2891	10	1.2919	55(0.0176,25)

[a] $F_N = (1/|\overline{\Delta 2\theta}|)(N_o/N_p)$, where N_p is the number of independent diffraction lines possible up to the N th observed line. $|\overline{\Delta 2\theta}|$ is the average absolute discrepancy value. 2θ is in (°) and d-values are in A.

Nelson–Riley extrapolation function to calculate the lattice constant and its standard deviation. Only one out of the 24 observed lines had $\Delta 2\theta > 0.03°$ and that was 0.05° (see Table I).

Comparison and Results

The comparison of lattice constants between this work and that of Güdel [2] and Ferrari *et al.* [4] are respectively 10.961(3) Å for $Cd_3[Cr(CN)_6]_2 \cdot 14H_2O$, 10.899(4) Å for $Cd_3[Cr(CN)_6]_2 \cdot xH_2O$ where x is $12 < x < 15$ and 10.953(30) Å for $Cd_3[Cr(CN)_6]_2 \cdot 6H_2O$. A further comparison can be made between X-ray powder and preliminary single-crystal diffraction data (obtained in this laboratory) of the title compound, 10.961(3) and 10.961(2) Å, respectively.

The criterion used for evaluating the reliability and for rating the quality of the powder diffraction pattern and indexing is the quantitative figure of merit, F_N, proposed by Smith and Snyder [5]. The F_N value is in units of reciprocal degrees which allows easy interpretation of published results. In this work, $F_{24} = 55(0.0176,25)$, meaning an average discrepancy in 2θ of $\leqslant 0.02$. A line-by-line evaluation leading to the cumulative function F_N is also reported in Table I. The overall quality figure of merit value, F_N, can be considered analogous to the R-value used in single-crystal structural analysis. The mean deviation between the observed and calculated d-spacing values is approximately 0.1%.

Controlled temperature and humidity permitted the crystal growth of the tetradecahydrated cyanide complex. Future work related to single-crystal analysis has been initiated and is expected to be forthcoming. The controlled hydration of zeolitic type compounds has fostered and renewed our interest in cadmium(II) hexacyanochromate(III) hydrate.

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