

SHORT COMMUNICATIONS

METAL PSEUDOHALIDE COMPLEXES, XIX
STRUCTURAL CHARACTERIZATIONS OF $Mn(PYRIDINE)_2(N_3)_2$
FROM ITS X-RAY POWDER DIFFRACTION PATTERN

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ABSTRACT. Application of the X-ray powder photograph automatic indexing program on the data obtained from X-ray powder diffraction pattern of $Mn(pyridine)_2(N_3)_2$ shows the complex to be crystallized in the tetragonal system, space group I and unit cell dimensions: $a = b = 15.698 \pm 0.03 \text{ \AA}$, $c = 10.147 \pm 0.04 \text{ \AA}$ and $V = 2500.7 \text{ \AA}^3$. On the other hand comparison of the powder diffraction pattern with that of the isomorphous compound $Cd(pyridine)_2(N_3)_2$, known to be crystallized in tetragonal system, space group $I_{41}A$, gives: $a = b = 15.70 \pm 0.03 \text{ \AA}$, $c = 10.17 \pm 0.05 \text{ \AA}$ and $V = 2509 \text{ \AA}^3$ for the unit cell parameters of $Mn(pyridine)_2(N_3)_2$. The number of formula units calculated from experimental density is $Z=8$. These results suggest that the complex contains the manganese atoms in an octahedral environment of six nitrogen atoms, four of them are end atoms of azide group, while the other two are nitrogen atoms of pyridine rings.

INTRODUCTION

Through the last two decades a number of programs for computer indexing of X-ray powder photographs have been developed (1-5). The availability of these programs heralded the possibility of structure determination of copper (II) complexes for which single crystals are hard to crystallize (6).

In a previous paper [7] we have described the preparation and characterization of some manganese (II) azido complexes of pyridine derivative ligands. One of these complexes, namely $Mn(pyridine)_2(N_3)_2$ has been found to be isomorphous with the corresponding cadmium(II) complex whose structure has been studied by means of X-ray single crystal analysis [8].

In this work an X-ray powder photograph automatic indexing program [9] has been used to index the X-ray powder diffraction diagram of $Mn(pyridine)_2(N_3)_2$ and to determine the unit cell dimensions. These data are then compared with those obtained from comparing the X-ray powder diagrams of both $Mn(pyridine)_2(N_3)_2$ and $Cd(pyridine)_2(N_3)_2$. The results of these two analyses are presented in this work.

EXPERIMENTAL

Preparation of the complexes. $Cd(pyridine)_2(N_3)_2$ has been prepared as recommended by Agrell [8], as colorless crystals. Elemental percentage analysis results of compound $C_{10}H_{10}N_8Cd$ are as follows (% found with calculated values between parenthesis): C : 33.58 (33.87), H: 3.02 (2.85), N: 32.08 (31.85) and Cd: 31.50 (31.70).

$Mn(pyridine)_2(N_3)_2$ was prepared by mixing an ethanolic solution of 10 mmol

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of pyridine and an aqueous solution of 3 mmol of $MnCl_2 \cdot 4H_2O$ followed by addition of NaN_3 (5.5 mmol). The final clear solution mixture was allowed to stand over several days in a dark place to produce the complex as colorless crystals. Elemental analysis results of empirical formula $C_{10}H_{10}N_8Mn$ (% found with calculated values in parenthesis): C: 40.52 (40.42) H: 3.63 (3.40), N: 37.82 (37.70) and Mn: 18.52 (18.48).

Physical measurements. X-ray powder diffraction patterns were taken using a Philips (PW 1010) X-ray powder diffraction spectrometer with $CuK\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). Elemental analysis and other physical measurements were made as given previously [7].

Data analysis. Two methods of analysis have been adopted in the present work. First we applied a powder diagram indexing routine developed by Taupin [9]. This is to find the lattice parameters and eventually the lattice type of an unknown specimen, knowing its accurate Debye-Scherrer diagram.

The data analysis was carried out using an IBM/XT compatible computer of 640 Mb RAM and 8087-2 arithmetic coprocessor and 10 MHz clock speed. An indexing run for the current case required about 11 min execution time, for the tetragonal type only.

In the second method a comparison of diagram of the $Mn(pyridine)_2(N_3)_2$ with that of $Cd(pyridine)_2(N_3)_2$ leads to the conclusion that they are isomorphous (Fig. 1). By comparing the two diagrams it was possible to index the different lines in the $Mn(pyridine)_2(N_3)_2$. The indexed lines were then fitted to the well known equation

$$\frac{1}{d} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

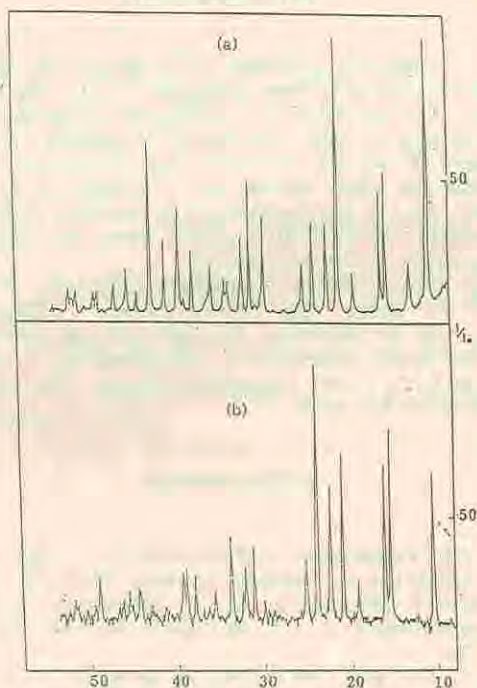


Fig. 1. X-ray powder diffraction of: a - $Cd(pyridine)_2(N_3)_2$
b - $Mn(pyridine)_2(N_3)_2$.

RESULTS AND CONCLUSIONS

For the present case the maximum unit cell volume was set at 2800 \AA^3 and the threshold figure of merit was set at 50, 12 weak lines were marked as possible extraneous. By testing the experimental diagram against all of the common lattice types except the triclinic a unique solution was found which is the I-tetragonal, with a final figure of merit 64.3 and no lines rejected. Standard deviation of 2θ values is 0.1. Table 1 shows a summary of the indexing results, together with the results of isomorphous study of the above mentioned compounds [8]. From the Table the values of 2θ and the d spacing are presented. It is clear from the Table that the indexing by the two methods are identical except for a few lines of very weak intensities.

Table 1. The results of automatic indexing compared with isomorphous assignment.

Cd(Pyridine) ₂ (N ₃) ₂ Standard			Cd(Pyridine) ₂ (N ₃) ₂ Experimental			Mn(Pyridine) ₂ (N ₃) ₂ Experimental			Isomorphous Assignment	
No	Meas. Calc.	h k l	No	2 θ Meas. Calc.	h k l	No	2 θ Meas. Calc.	h k l	No	h k l
1	10.36 10.35	1 0 1	1	10.39 10.28	1 0 1	1	10.35 10.37	1 0 1	1	1 0 1
2	15.27 15.26	2 1 1	2	15.20 15.15	2 1 1	2	15.24 15.33	2 1 1	2	2 1 1
3	15.85 15.85	2 2 0	3	15.80 15.73	2 2 0	3	15.89 15.95	2 2 0	3	2 2 0
4	18.96 18.97	3 0 1	4	18.95 18.83	3 0 1	4	18.95 19.06	3 0 1	4	3 0 1
5	20.77 20.78	2 0 2	5	20.70 20.64	2 0 2	5	20.77 20.82	2 0 2	5	2 0 2
6	22.07 22.07	3 2 1	6	21.90 21.91	3 2 1	6	22.10 22.19	3 2 1	6	3 2 1
7	23.65 23.66	2 2 2	7	23.49 23.50	2 2 2	7	23.70 23.74	2 2 2	7	2 2 2
8	24.82 24.81	4 1 1	8	24.70 24.63	4 1 1	8	25.10 24.95	4 1 1	8	4 1 1
9	24.97 24.99	3 2 1	9	24.81 24.79	3 2 1		25.07	3 1 2		
10	26.93 26.92	1 0 3	10	26.80 26.75	1 0 3	9	26.89 26.94	1 0 3	9	1 0 3
11	29.23 29.24	2 1 3	11	29.10 29.05	2 1 3	10	29.19 29.28	2 1 3	10	2 1 3
12	29.58 29.73	3 3 2				11	29.90 29.86	3 3 2		
	29.58	4 3 1	12	29.89 29.36	4 3 1		29.76	4 3 1	11	4 3 1
13	30.80 30.81	4 2 2	13	30.70 30.59	4 2 2	12	30.99 30.95	4 2 2	12	4 2 2
14	32.01 31.72	5 2 1	14	31.55 31.48	5 2 1	13	32.00 31.91	5 2 1	13	5 2 1
15	32.01 32.02	4 4 0				14	32.40 32.23	4 4 0	14	4 4 0
16	33.42 33.43	3 2 3	15	33.20 33.20	3 2 3	15	33.59 33.52	3 2 3	15	3 2 3
			16	33.59 33.62	5 1 2					
				33.75	6 0 0					
17	33.36 35.33	0 0 4	17	35.10 35.11	0 0 4	16	35.50 35.35	0 0 4		
	35.36	4 1 3					35.46	4 1 3	16	4 1 3
18	35.65 35.65	6 1 1	18	35.29 35.38	6 1 1				17	6 1 1
						17	36.20 36.29	1 1 4		
							36.16	6 2 0		
19	35.93 35.92	6 2 0	19	35.50 35.64	6 2 0				18	6 2 0
						18	36.90 36.89	4 4 2		
20	37.48 37.60	5 3 2	20	37.20 37.32	5 3 2	19	37.75 37.79	5 3 2		
	37.48	5 4 1		37.19	5 4 1		37.71	5 4 1	19	5 4 1
21	38.49 38.48	6 0 2	21	38.20 38.19	6 0 2	20	38.69 38.68	6 0 2	20	6 0 2
22	38.96 38.95	2 2 4	22	38.70 38.69	2 2 4	21	39.10 39.00	2 2 4		
	38.97	4 3 3		38.69	4 3 3		39.11	4 3 3	21	4 3 3
23	39.24 39.24	6 3 1	23	38.93 38.89	6 3 1	22	39.40 39.48	6 3 1	22	6 3 1
24	40.66 40.67	5 2 3	24	40.35 40.37	5 2 3	23	40.80 40.83	5 2 3	23	5 2 3
							40.60	5 5 0		
25	40.93 40.93	7 0 1				24	41.10 41.19	7 0 1	25	7 0 1
26	42.31 42.29	4 0 4	25	41.99 42.01	4 0 4	25	42.60 42.38	4 0 4	26	4 0 4
27	42.56 42.57	7 2 1					44.10	6 1 3	27	7 2 1
28	43.91 43.89	4 2 4	26	43.50 43.59	4 2 4	27	44.00 44.00	4 2 4		
	43.91	6 1 3		43.58	6 1 3		44.10	6 1 3	28	6 1 3
							43.88	7 3 0		
29	45.04 44.98	1 0 5	27	44.70 44.69	1 0 5					
	45.03	6 4 2				28	44.40 44.51	5 5 2		
30	45.45 45.46	5 4 3				29	45.35 45.29	6 4 2	29	6 4 2
31	45.70 45.70	6 5 1	28	46.10 46.20	6 5 1	30	46.00 45.99	6 5 1	30	6 5 1

For the present case the maximum unit cell volume was set at 2800 \AA^3 and the threshold figure of merit at 20. By testing the experimental diagram against all the common lattice types except the triclinic, a unique solution was found which is the 1 - tetragonal, with the final figure of merit 64 and no lines were rejected. Table 1 shows a summary of the indexing results, together with the results of isomorphous study of the above mentioned compounds [8]. The table lists a comparative results for four cases. The first is the indexing results of a standard data for $\text{Cd}(\text{pyridine})_2(\text{N}_3)_2$. The next group is for a locally prepared and measured sample under the same conditions. The next group is for $\text{Mn}(\text{pyridine})_2(\text{N}_3)_2$. The last group is the results of isomorphous assignment. From the Table, it is clear that the results of standard $\text{Cd}(\text{pyridine})_2(\text{N}_3)_2$ and that of locally prepared sample are identical in 6 out of 31 peaks. The same is applied to the $\text{Mn}(\text{pyridine})_2(\text{N}_3)_2$, except of peak No. 26, which is assigned to the 334 plane. As for the isomorphous assignment, the results are fairly identical to that from automatic indexing except in the region of peaks 16-17.

The unit cell dimensions calculated by the program are: $a = b = 15.698 \pm 0.03 \text{ \AA}$, $c = 10.147 \pm 0.04 \text{ \AA}$ and $V = 2500.7 \text{ \AA}^3$. The corresponding values calculated from the tetragonal equation are: $a = b = 15.70 \pm 0.03 \text{ \AA}$, $c = 10.17 \pm 0.05 \text{ \AA}$ and $V = 2509 \text{ \AA}^3$.

It is clear that the parameters obtained from both methods of analysis are very close except that the c value as determined by automatic indexing is a little bit smaller than that obtained from the tetragonal equation. The difference in unit cell volume is smaller than that found for the $\text{Cd}(\text{pyridine})_2(\text{N}_3)_2$ [2]. This may be attributed to the difference in size of $\text{Cd}(\text{II})$ and $\text{Mn}(\text{II})$ ions.

The density of $\text{Mn}(\text{pyridine})_2(\text{N}_3)_2$ as determined experimentally was found to be $1.55605 \text{ gm. cm}^{-3}$. Accordingly the number of formula units per unit cell is $Z = 8.01$. Thus the unit cell contains 8 formula units similar to that found in $\text{Cd}(\text{pyridine})_2(\text{N}_3)_2$. These results suggest that in the structure of the title complex, like that of $\text{Cd}(\text{pyridine})_2(\text{N}_3)_2$ the Mn atom is surrounded by an octahedral configuration of six nitrogen atoms (Fig. 2). Four of the surrounding nitrogen atoms are end atoms of azide groups, while the other two are nitrogen atoms of pyridine rings. The structure can be visualized as being built by linking of the Mn octahedra, through four corners, by azido groups to form a three dimensional network. The pyridine rings are attached to the two remaining corners of the octahedra. The azide groups are linear, symmetrical and coordinated at each end to a different Mn atom.

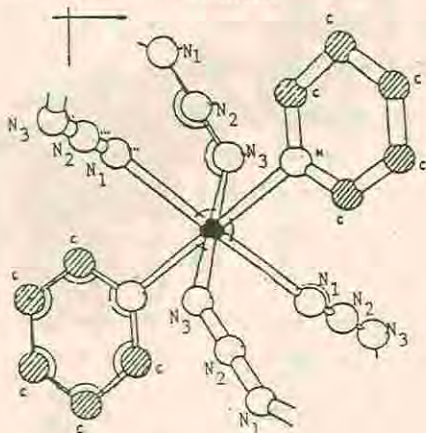


Fig. 2. Expected structure of $\text{Mn}(\text{pyridine})_2(\text{N}_3)_2$.

In summary, the results obtained in this work confirm the value of X-ray automatic powder photograph indexing program for the determination of the unit cell dimensions, as well as the lattice type of an unknown sample. The parameters obtained by Taupin program are almost the same as calculated from isomorphous analysis. Application of the above mentioned program for analysis of other complexes are in progress.

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