X-ray powder diffraction data for methylene bis(thiocyanate) $CH_2(SCN)_2$, a microbicide for water-treatment purposes

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X-ray powder diffraction data, unit-cell parameters, and space group for methylene bis(thiocyanate) ($C_3H_2N_2S_2$) are reported [$a = 6.6888(4)$ Å, $b = 8.0616(6)$ Å, $c = 11.089(1)$ Å, $\beta = 105.33(1)$, $Z = 4$, unit-cell volume $V = 576.68(7)$ Å^3, with $M_{20} = 56.0$ and $F_{30} = 43.8$ (0.0079, 87)]. All measured lines were indexed and are consistent with the monoclinic *I*2/*c* space group. © *2014 International Centre for Diffraction Data*. [doi:10.1017/S0885715614001122]

Key words: X-ray powder diffraction, methylene bis(thiocyanate), biocide, microbicide

I. INTRODUCTION

A biocide is a chemical substance or microorganism, which can deter, render harmless, or exert a controlling effect on any harmful organism by chemical or biological means, and therefore are commonly used in medicine, agriculture, forestry, and industry. In particular, methylene bis(thiocyanate) (MBT, Figure 1) is a microbiocidal agent mainly used in industrial water cooling systems and paper mills as an inhibitor of algae, fungi, and bacteria (Braun *et al.*, 2006). The crystal structure of MBT was studied from single-crystal X-ray diffraction (Konnert and Britton, 1971) and is reported in the CSD-database with refcode MEDTCN (Allen, 2002; CSD, version 5.35, February).

This compound crystallize in the monoclinic space-group *I*2/*c* (No. 15), a non-standard setting of *C*2/*c* (No. 15), with $a = 6.667(11)$ Å, $b = 8.042(13)$ Å, $c = 11.101(19)$ Å, and $\beta = 105.25(25)°$. Recently, experimental and theoretical vibrational studies using density functional theory (DFT) calculation was performed for this molecule (Fernández *et al.*, 2013). However, an experimental X-ray powder diffraction pattern for MBT has not been reported in the PDF-database (ICDD, 2011). In this paper, we present powder X-ray diffraction data for well-synthesized MBT.

II. EXPERIMENTAL

A. Synthesis

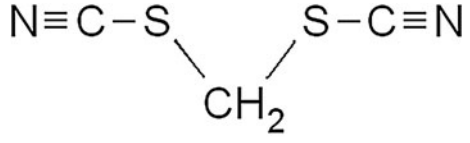
MBT was prepared reacting sodium thiocyanate (NaSCN) and methylene bromide (CH_2Br_2), following a procedure reported in the literature (Muthusubramanian *et al.*, 2003). MBT, an organosulfur compound, is a yellow granular solid with sulfur-like smell (m.p. 102–104 °C).

B. Fourier-transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopy

The FTIR absorption spectrum was obtained as KBr pellet using a Perkin-Elmer 1600 spectrometer. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance 400 model spectrometer in DMSO-d_6 solution. Infrared spectrometry showed stretching vibrations; 3017, 2956, and 1380 cm^{-1} (CH_2), 2168 cm^{-1} (C–N), 867 cm^{-1} (S–C–S), 700 cm^{-1} (S–CN), and NMR; ^{1}H NMR (400 MHz, DMSO-d_6) $\delta =$ 4.92 (s, H_2). ^{13}C NMR (100.6 MHz, DMSO-d_6) $\delta = 119.16$ (**C**N), 37.88 (**C**H_2).

C. X-ray powder diffraction data

For the X-ray analysis, a small quantity of the sample was ground mechanically in an agate mortar and pestle. The resulting fine powder, sieved to 106 μm, was mounted on a flat zero-background holder covered with a thin layer of petroleum jelly. The X-ray powder diffraction data were collected at room temperature 293(1) K, in θ/θ reflection mode using a Philips diffractometer with PW-1150/25 goniometer and monocromatized Cu$K\alpha$ radiation ($\lambda = 1.5406$ Å). The diffractometer was operated at 40 kV and 25 mA. The specimen was scanned from 10° to 80°2θ, with a step size of 0.02° and counting time of 10 s per step. Silicon (SRM 640) was used as an external standard. The analytical software package WinPLOTR (Roisnel and Rodríguez-Carvajal, 2001) was



MBT

Figure 1. Structural formula of methylene bis(thiocyanate).

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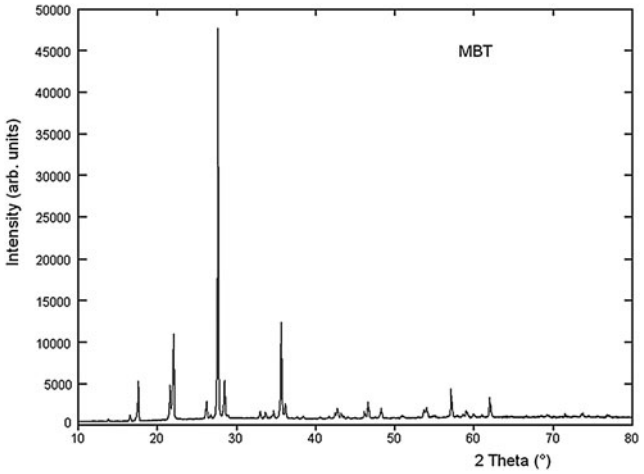

Figure 2. X-ray powder diffraction pattern of methylene bis(thiocyanate).

TABLE I. X-ray powder diffraction data of methylene bis(thiocyanate).

$2\theta_{obs}$ (°)	d_{obs} (Å)	$(I/I_o)_{obs}$	h	k	l	$2\theta_{cal}$ (°)	d_{cal} (Å)	$\Delta 2\theta$ (°)
13.741	6.4387	1	0	1	1	13.744	6.4375	0.003
16.555	5.3502	2	0	0	2	16.564	5.3474	0.009
17.579	5.0407	11	−1	1	0	17.593	5.0368	0.014
21.566	4.1170	9	−1	1	2	21.578	4.1148	0.012
22.018	4.0335	22	0	2	0	22.033	4.0308	0.015
26.199	3.3985	4	−1	2	1	26.211	3.3970	0.012
26.682	3.3381	1	1	1	2	26.678	3.3386	−0.004
27.627	3.2260	100	2	0	0	27.632	3.2254	0.005
28.467	3.1327	10	1	2	1	28.480	3.1313	0.013
28.890	3.0878	1	−2	1	1	28.896	3.0871	0.006
32.946	2.7163	2	2	1	1	32.952	2.7158	0.006
33.657	2.6605	1	−1	2	3	33.657	2.6605	0.000
34.546	2.5941	2	−1	1	4	34.552	2.5937	0.006
35.610	2.5190	22	−2	2	0	35.619	2.5184	0.008
36.118	2.4847	4	2	0	2	36.092	2.4864	
			−2	2	2	36.120	2.4846	0.002
37.575	2.3916	1	−2	0	4	37.561	2.3925	−0.014
38.385	2.3430	1	−1	3	2	38.385	2.3430	0.000
42.419	2.1291	1	−3	1	2	42.424	2.1288	0.005
42.689	2.1162	3	2	2	2	42.690	2.1162	0.001
43.149	2.0947	1	−2	3	1	43.161	2.0942	0.012
46.114	1.9667	3	2	3	1	46.127	1.9662	0.014
46.579	1.9481	4	−3	2	1	46.588	1.9478	0.009
			1	0	5	48.190	1.8867	
48.216	1.8857	2						
			0	4	2	48.212	1.8859	−0.004
			−2	4	0	53.572	1.7092	
53.594	1.7085	2						
			1	2	5	53.585	1.7088	−0.009
53.704	1.7053	1	−3	3	2	53.693	1.7056	−0.011
53.943	1.6983	1	−2	4	2	53.936	1.6985	−0.007
54.904	1.6708	1	−4	0	2	54.899	1.6709	−0.005
57.050	1.6130	1	4	0	0	57.059	1.6127	0.010
			0	4	4	57.188	1.6094	−0.012
57.200	1.6091	5						
			−4	1	3	57.230	1.6083	
57.789	1.5941	1	0	5	1	57.780	1.5943	−0.009
			−3	1	6	58.981	1.5647	0.008
58.972	1.5649	2						
			−1	5	0	59.000	1.5642	
59.860	1.5438	1	−4	2	2	59.868	1.5436	0.008
61.922	1.4972	4	4	2	0	61.918	1.4973	−0.004
62.093	1.4935	1	−3	4	1	62.086	1.4937	−0.007
68.451	1.3694	1	−2	0	8	68.439	1.3697	−0.013
69.125	1.3577	1	4	2	2	69.115	1.3579	−0.010
71.447	1.3192	1	−5	1	2	71.439	1.3193	−0.009
73.762	1.2834	1	−3	1	8	73.775	1.2832	0.013
74.408	1.2739	1	5	1	0	74.402	1.2739	−0.005
76.789	1.2402	1	2	6	0	76.782	1.2403	−0.007
76.784	1.2401	1	−4	4	4	76.784	1.2403	0.011
76.784	1.2401	1	−4	4	4	76.784	1.2403	0.011

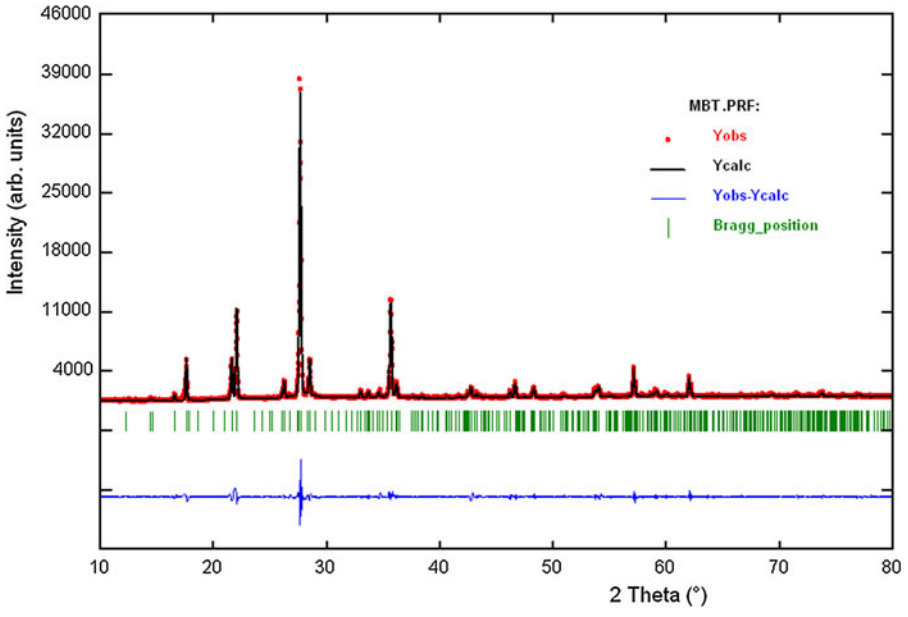

Figure 3. (Color online) Le Bail refinement of methylene bis(thiocyanate).

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used to establish the positions of the peaks and to determine the peak intensities of the diffraction peaks.

III. RESULTS AND DISCUSSION

The X-ray powder pattern of MBT is shown in Figure 2. The 20 first peak positions were indexed using the program DICVOL06 (Boultif and Louër, 2004), which gave a unique solution in a monoclinic cell. The systematic absences study (*hkl*: $h + l = 2n$) indicated an *I*-type cell consistent with the reported crystal structure (Konnert and Britton, 1971). The complete powder diffraction dataset was reviewed in the monoclinic space group *I*2/*c*, using the program NBS*AIDS83 (Mighell *et al.*, 1981). All measured lines were indexed and were consistent with the monoclinic space group *I*2/*c* (No. 15). From this analysis, the refined unit-cell parameters obtained were: $a = 6.6888(4)$ Å, $b = 8.0616(6)$ Å, $c = 11.089(1)$ Å, $\beta = 105.33(1)$, $V = 576.68(7)$ Å^3, and $Z = 4$, with figures of merit $M_{20} = 56.0$ (de Wolff, 1968) and $F_{30} = 43.8$ (0.0079, 87) (Smith and Snyder, 1979). The resulting X-ray powder diffraction data for MBT, together with the observed and calculated 2θ, the *d*-spacing's as well as the relative intensities of the reflections, are given in Table I. In order to confirm the unit-cell parameters, an Le Bail refinement (Le Bail, 2005) of the whole diffraction pattern without the structural model was carried out using the FULLPROF program (Rodríguez-Carvajal, 2013). Figure 3 shows a very good fit between the observed and calculated patterns.

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SUPPLEMENTARY MATERIALS AND METHODS

The supplementary material for this article can be found at http://www.journals.cambridge.org/PDJ

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