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The structure of calomel, Hg_2Cl_2, derived from neutron powder data

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Powder structure / Mercury(I) chloride

Abstract. Hg_2Cl_2, M = 472.1 Daltons, tetragonal, *I4/mmm*, a = 4.4795(5) Å, c = 10.9054(9) Å, V = 218.83(8) Å^3, Z = 2, D_c = 7.162 g cm^{-3}, λ(neutron) = 1.893 Å, R_B = 0.026, R_P = 0.043. The structure of Hg_2Cl_2 was refined using the Rietveld profile fitting technique on neutron powder data. Parameters obtained were comparable to single crystal X-ray results.

Introduction

Havighurst (1926) reported the structures of Hg_2Cl_2, Hg_2Br_2, and Hg_2I_2. Further work was carried out by Grdenic and Djordjevic (1956) on the fluoride. Dorm (1971), using single crystal methods, reinvestigated the structures of the fluoride, chloride and iodide to determine if there was a correlation between the Hg–Hg bond length and the electronegativity of the ligand. The neutron powder data were collected for calomel, Hg_2Cl_2, to verify its structure.

Experimental method

A powder sample of Hg_2Cl_2 (laboratory reagent grade) was packed in a 5 mm diameter V canister and mounted on the High Resolution Powder Diffractometer (HRPD) at the HIFAR facility at Lucas Heights, Australia.

Table 1. Crystal structure and parameters for Hg_2Cl_2. Space group: $I4/mmm$.

	Havighurst (1926)	Dorm (1971)	This study
a (Å)	4.47	4.482(2)	4.4795(5)
c (Å)	10.89	10.910(3)	10.9054(9)
Hg_z	0.110	0.1158(3)	0.119(1)
β_{11}		0.0270(3)	0.0001(7)
β_{33}		0.0019(5)	0.071(5)
Cl_z	0.360	0.3380(4)	0.3356(8)
B_{iso} (Å^2)		3.6(7)	
β_{11}			0.056(7)
β_{33}			−0.004(1)
R_B		0.08	0.0255

Table 2. Bond distances (Å) and angles (°) for Hg_2Cl_2.

	Dorm (1971)	This study
Hg−Hg	2.526(6)	2.5955(2)
Hg−Cl	2.43(4)	2.3622(2)
Hg ... Cl	3.209(6)	3.2059(3)
Cl−Hg ... Cl		81.12(5)
Cl ... Hg ... Cl		88.63(5)

The neutron diffraction pattern (Ge monochromated neutrons, 1.893 Å) was measured [2θ, 7.097° to 126.396°, in 0.1° steps, monitor count, 5×10^4 neutrons]. The structure was refined using Hill's and Howard's (1985) version of the computer program DBW 3.2 by Wiles and Young (1981).

Discussion

The neutron powder pattern of Hg_2Cl_2 has a noisy background in which there is, especially in the tail regions, an uncertainty with peak shapes.[1] Consequently, a general Voigtian peak shape function of Suortti et al. (1979) was used and this provided a good fit for the observed profile. The large number of observations (8 counters, 1000 observations per counter) offset the relatively weak intensities which were obtained because the neutron monitor counter was set to 5×10^4. According to Hill and Madsen (1986), R_p and R_{wp} are independent of scan point density but dependent on counting statistics. G of F (Goodness of Fit), and cell dimensions are unaffected. When errors are dependent on experimental conditions, e.g. preferred orientation, variation in incident beam intensity, crystal defects, and deficiencies in the structural model, or the diffraction peak model, the

[1] Additional material to this paper can be ordered from the Fachinformationszentrum Energie-Physik-Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG. Please quote reference no. CSD 53503, the names of the authors and the title of the paper.

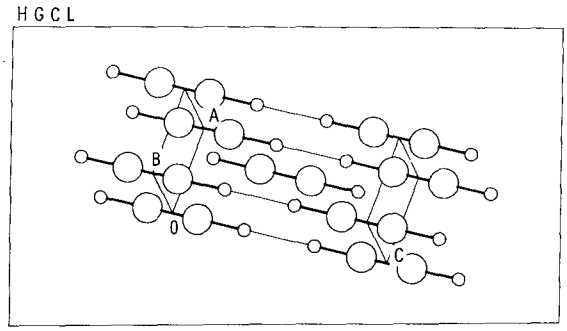

Fig. 1. Packing diagram for calomel.

Durbin-Watson d statistic will be significant. It will be less important as the counting statistics become less favourable. $R_B = 0.0255$, G of F (ideally 1.00) 15.48 (due to noisy background), $1.85 < d < 2.15$ at 99.9% confidence level but $d = 1.46$, therefore negative serial correlation (Durbin and Watson, 1950), $R_p = 0.0431$, $R_{wp} = 0.0525$, (Table 1). This indicated that the Rietveld technique could provide a structure solution from a powder diffraction profile on highly absorbing samples. Hg_2Cl_2 was refined using Havighurst's parameters. Data were corrected for absorption, $\mu R = 0.70$. The results agreed well with the X-ray structure (Dorm, 1971), (Figure 1, Table 2). The scattering lengths used for Hg and Cl were 12.660 and 9.579 fm^{-1} respectively.

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