

Crystal Structure and Optical Properties of 4-[4-(Dimethylamino)-styryl]-1-methyl-pyridinium Lead Tribromide

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The title compound crystallizes in the centrosymmetric space group $I2/a$. When pumped by 458 and 1064 nm laser radiation the compound gives rise to a broad luminescence band at ca. 668 and 671 nm, respectively.

Key words: Metal Halides, Organic-Inorganic Hybrids,
Optical Properties

Recently, the preparation and optical properties of $[\text{DSM}]\text{PbI}_3 \cdot 2\text{DMSO}$ (where DMS is *trans*-4-[4-(dimethylamino-styryl)-1-methyl-pyridinium ion, and DMSO is dimethyl sulfoxide) [1] and similar compounds [2, 3] have been reported. Moreover, the crystal structure of $[\text{DSM}]\text{PbI}_3 \cdot 2\text{DMSO}$ has been described [1]. This compound crystallizes in the monoclinic non-centrosymmetric space group Ic . When pumped by 1064 nm laser radiation, it gives rise to both a large second harmonic generation (SHG) signal at 532 nm and a broad red luminescence around 650 nm [1].

In this paper, the crystal structure and the photoluminescence (PL) properties of $[\text{DSM}]\text{PbBr}_3$ are described.

Experimental Section

Single crystals suitable for X-ray diffraction and PL measurements were prepared by modification of the method reported in [2], as follows: A hot solution of $[\text{DSM}]\text{Br}$ (255 mg, 0.8 mmol) in CH_3CN (100 ml) was mixed with a hot solution of PbBr_2 (223.6 mg, 0.8 mmol) and Bu_4NBr (644 mg, 1 mmol) in CH_3CN (100 ml). After slow cooling to r.t. a

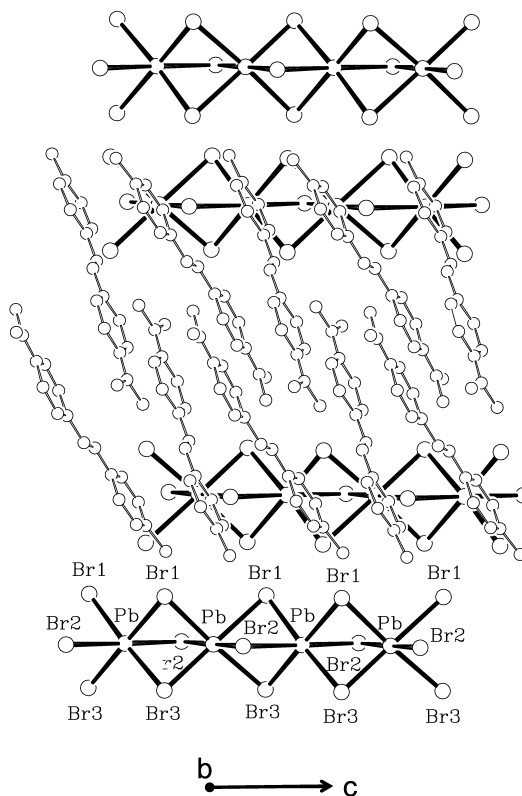


Fig. 1. Packing diagram of $[\text{DMS}]\text{PbBr}_3$, showing the labeling of the inorganic layer.

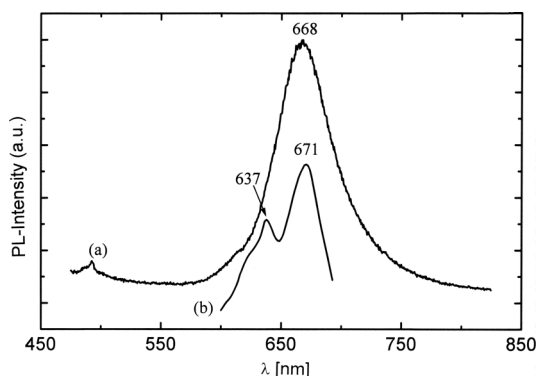


Fig. 2. PL spectra of $[\text{DMS}]\text{PbBr}_3$, single crystals with 458 nm laser excitation (a) and 1064 nm laser excitation (b).

precipitate of brown-golden elongated plates was obtained; it was filtered, washed with acetone and air dried: yield 303–364 mg (55–66%). $\text{C}_{16}\text{H}_{19}\text{N}_2\text{Br}_3\text{Pb}$ (686.25): calcd. C 27.99, H 2.77, N 4.08, Br 34.98; found C 28.02, H 2.80, N 4.01, Br 34.92.

Crystal structure data. – $\text{C}_{16}\text{H}_{19}\text{N}_2\text{Br}_3\text{Pb}$, $M = 686.25$, $F(000) = 2528$, red-golden elongated plates, monoclinic system, $a = 37.23(1)$, $b = 13.523(6)$, $c = 7.834(3)$ Å, $\beta = 90.50(1)^\circ$, $V = 3944(3)$ Å³, space group $I2/a$, $Z = 8$, $D_c = 2.312$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 14.632$ mm⁻¹. The intensities were collected on a Crystal Logic Dual Goniometer diffractometer, with graphite - monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) and ω - 2θ -scan technique [$T = 298$ K; $-42 \leq h \leq 39$, $0 \leq k \leq 15$, $0 \leq l \leq 9$; θ -range for data collection = 2.19 to 24.25°]. The structure was solved by direct methods using SHELXS-86 [4] and refined by full-matrix least-squares techniques on F^2 with SHELXL-93 [5] using 3163 reflections and refining 255 parameters. All hydrogen atoms (except those of the methyl groups C1 and C16 which were introduced at calculated positions as riding on bonded atoms) were located by difference maps and were refined isotropically. All non-H atoms were refined anisotropically. Final R indices [$I > 2\sigma(I)$] were $R = 0.0317$ and $wR = 0.0760$. Full crystallographic data are available from the authors and have been deposited at the Cambridge Crystallographic Data Centre under deposition number CCDC 208748.

Results and Discussion

As illustrated by the packing diagram of Fig. 1, the structure consists of face-sharing PbBr_6 octahedra [$\text{Pb-Br}(1)\text{-Pb} = 78.95(3)$, $\text{Pb-Br}(2)\text{-Pb} = 78.64(4)$, $\text{Pb-Br}(3)\text{-Pb} = 81.94(3)^\circ$] forming one-dimensional chains along the c axis. The Pb-Br bond distances range from $2.934(1)$ to $3.147(1)$ Å.

The long axis of the elongated plates of the compound is almost parallel to the c axis *i. e.*, almost parallel to the $(\text{PbBr}_3)_n$ -chain direction. PL spectra were observed in single crystals as well as in thin deposits of the compound on quartz plates. The PL intensity of $(\text{DSM})\text{PbBr}_3$, in comparison to that of $(\text{DSM})\text{Br}$, is es-

timated by using deposits of compounds of the same optical density at 484 nm [2].

Fig. 2 shows the PL spectra of a single crystal of $(\text{DSM})\text{PbBr}_3$. Similar spectra were observed for thin deposits on quartz plates. With a 458 nm laser excitation the complex exhibits a PL band at 668 nm arising from the organic part of this hybrid compound. Similar spectra have been observed from analogous compounds based on isomers of DSM [2, 3]. In the present case of $(\text{DSM})\text{PbBr}_3$, the PL band (Fig. 2(a)) seems to be more than three times stronger than that of $(\text{DSM})\text{Br}$. Perhaps, this is a consequence of the “heavy-counterion” effect, *i. e.*, a kind of process effected in the organic units in the presence of a big inorganic network, like the “heavy-atom” effect (see [6, 7] and refs cited therein). A similar effect was observed in the PL spectra of $[\text{C}_{10}\text{H}_7\text{CH}_2\text{NH}_3]\text{PbI}_3$ and related one-dimensional compounds [3, 8–11]. The PL spectrum of $[\text{C}_{10}\text{H}_7\text{CH}_2\text{NH}_3]\text{PbI}_3$, for example, exhibits only a phosphorescence band around 500 nm [8, 10, 11]. With a 1064 nm laser excitation $(\text{DSM})\text{PbBr}_3$ exhibits also a PL band at *ca.* 671 nm (Fig. 2(b)). Although $(\text{DSM})\text{PbBr}_3$ crystallizes in a centrosymmetric space group, it gives rise to SHG radiation, which can be re-absorbed and converted into the red luminescence (at *ca.* 671 nm). A similar effect has been observed in *trans*-stilbazole, which crystallizes in the centrosymmetric space group $P2_1/c$ [12]. The compounds of the type $[\text{C}_{10}\text{H}_7\text{CH}_2\text{NH}_3]\text{PbI}_3$ (with a non centrosymmetric space group $P2_1$) do not exhibit this effect. However, at the moment we do not have facilities in our laboratories for further investigations of compounds of the type $(\text{DSM})\text{PbX}_3$ ($X = \text{Br}, \text{I}$).

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