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Crystal structure of dibromido-(1-methyl-1*H*-imidazole- κ^1N)-(3-(3-methyl-1*H*-imidazol-3-ium-1-yl)propanoato- κ^1O)zinc(II), $C_{11}H_{16}Br_2N_4O_2Zn$

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.22 × 0.19 × 0.15 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	6.64 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	26.0°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	4151, 2086, 0.029
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1845
$N(\text{param})_{\text{refined}}$:	181
Programs:	Bruker [1], SHELX [2, 3], Olex2 [4], Diamond [5]

Figure 1: The asymmetric unit of the title compound.

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Abstract

$C_{11}H_{16}Br_2N_4O_2Zn$, monoclinic, Cc (no. 9), $a = 15.534(7)$ Å, $b = 7.956(4)$ Å, $c = 14.589(7)$ Å, $\beta = 119.094(8)^\circ$, $V = 1575.5(13)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0296$, $wR_{\text{ref}}(F^2) = 0.0703$, $T = 296$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

All chemicals were available from commercial sources and used without further purification. 3-(3-Carboxy-propyl)-1-methyl-imidazolium bromide was synthesized according to the method reported in the literature [6]. Zinc (0.030 mmol), 3-(2-carboxy-propyl)-1-methyl-imidazolium bromide (0.020 mol) and 1-methylimidazole (0.010 mol) were dissolved in 50 mL water, and this mixture was stirred for 10 days at 50 °C. After filtration of the reaction mixture, the filtrate was concentrated to 10 mL. Slow evaporation at room temperature yielded block crystals after seven days.

Experimental details

The U_{iso} values were set to $1.5U_{\text{eq}}(C)$ for hydrogen atoms of all methyl groups and $1.2U_{\text{eq}}(C)$ for the other functional groups. All hydrogen atoms were placed in the idealized positions and refined using riding coordinates.

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Br1	0.23519 (6)	0.80205 (9)	1.13786 (5)	0.0599 (3)
Br2	0.23089 (5)	0.32299 (9)	1.15759 (5)	0.0523 (2)
C1	−0.3128 (6)	0.5418 (10)	0.3383 (7)	0.056 (2)
H1A	−0.315560	0.595234	0.277884	0.084*
H1B	−0.350220	0.439450	0.317294	0.084*
H1C	−0.339788	0.615641	0.369817	0.084*
C2	−0.1329 (7)	0.5382 (12)	0.4017 (7)	0.065 (2)
H2	−0.134754	0.588798	0.343335	0.078*
C3	−0.0522 (8)	0.4881 (16)	0.4869 (8)	0.079 (3)
H3	0.012395	0.497545	0.499795	0.095*
C4	−0.1787 (7)	0.4311 (8)	0.5051 (6)	0.0467 (18)
H4	−0.218054	0.392865	0.532549	0.056*
C5	−0.0188 (7)	0.3590 (10)	0.6588 (6)	0.059 (2)
H5A	0.037957	0.302672	0.662026	0.071*
H5B	−0.054479	0.278439	0.677582	0.071*
C6	0.0149 (7)	0.5032 (9)	0.7352 (6)	0.0457 (17)
H6A	−0.042365	0.553508	0.734323	0.055*
H6B	0.044566	0.587717	0.711388	0.055*
C7	0.0878 (5)	0.4567 (9)	0.8467 (5)	0.0387 (16)
C8	0.4647 (8)	0.4469 (12)	0.8745 (8)	0.071 (3)
H8A	0.533653	0.470010	0.902706	0.107*
H8B	0.453003	0.328988	0.859668	0.107*
H8C	0.427742	0.509789	0.810913	0.107*
C9	0.4942 (8)	0.5608 (12)	1.0469 (8)	0.063 (2)
H9	0.561158	0.584016	1.077059	0.076*
C10	0.4352 (6)	0.5847 (10)	1.0897 (6)	0.053 (2)
H10	0.455805	0.629304	1.156119	0.063*
C11	0.3447 (6)	0.4815 (9)	0.9380 (6)	0.0438 (17)
H11	0.290379	0.440056	0.878342	0.053*
N1	−0.2110 (5)	0.5039 (7)	0.4136 (4)	0.0403 (13)
N2	−0.0829 (5)	0.4204 (8)	0.5518 (5)	0.0481 (15)
N3	0.4342 (5)	0.4949 (8)	0.9497 (5)	0.0453 (14)
N4	0.3428 (5)	0.5355 (7)	1.0234 (5)	0.0399 (13)
O1	0.1200 (6)	0.3157 (8)	0.8674 (5)	0.093 (2)
O2	0.1133 (4)	0.5752 (6)	0.9098 (4)	0.0502 (13)
Zn1	0.22680 (6)	0.54721 (8)	1.04820 (6)	0.0365 (2)

Comment

Carboxyl-functional ionic liquids (COOH-ILs) have been attracting growing attention and are used for a variety of applications such as synthesis [6], catalysis [7, 8] and selective separation and extraction [9, 10] and so on. The structures of some COOH-ILs have also been experimentally and theoretically investigated [11–14]. For example, Fei et al. [6, 12] reported the imidazolium containing one or two carboxylic acid substituent groups with chloride, tetrafluoroborate and trifluoromethanesulphonate anion, and used them to construct stable coordination polymers [12]. Xuan et al. [13] determined the crystal structures of COOH-ILs with bromide, chloride, hexafluorophosphate and bis(trifluoromethylsulfonyl)imide anion and found a

difference in the hydrogen bonding network between the hydrophobic and hydrophilic COOH-ILs. In addition, the pH-dependent reversible crystal transformation from ILs to their zwitterions was found [11, 12, 15]. A further model study on a zwitterionic molecule [3-(3-methylimidazolium-1-yl)propanoate] has revealed a substantial conformational rearrangement [16]. Herein, we reported the crystal structure of the title coordination compound, which was prepared by slow evaporation from the reaction mixture, reacted with 3-(2-carboxy-propyl)-1-methyl-imidazolium bromide, 1-methylimidazole in a 2:1 M ratio with an excess of zinc powder.

In the case of the title compound as shown in Figure 1, a mononuclear zinc complex crystallizes in the non-centrosymmetric space group *Cc* with one independent zinc ion, one 1-methyl-1*H*-imidazole [17] molecule, one 3-(3-methyl-1*H*-imidazol-3-ium-1-yl)propanoate and two bromides in the asymmetric unit. The central Zn²⁺ is fourfold coordinated in a slightly distorted tetrahedral geometry. The Br1–Zn1 and Br2–Zn1 bond lengths are 2.3817 (11) and 2.3738(11) Å, respectively. The distance [2.006 (5)] between Zn1 and N4 is different to that [1.942 (4) Å] between Zn1 and O2. The angle of O2–Zn1–Br2 is about [119.97 (13)°], which is significantly larger than that of O2–Zn1–Br1 [104.74 (12)°]. The conformation of 3-(3-methyl-1*H*-imidazol-3-ium-1-yl)propanoate is similar to the structure reported in reference [16]. The weak C–H⋯Br and C–H⋯O hydrogen bonds and a C⋯Br short contact (3.549 Å) further stabilize the crystal.

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