Crystal structure of phenylpiperazinium tetrachlorozincate, $(C_{10}H_{16}N_2)[ZnCl_4]$

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Abstract

$C_{10}H_{16}Cl_4N_2Zn$, monoclinic, $P12_1/c1$ (no. 14), $a = 7.768(3)$ Å, $b = 20.393(3)$ Å, $c = 9.615(6)$ Å, $\beta = 104.75(4)^\circ$, $V = 1473.0$ Å³, $Z = 4$, $R_{gt}(F) = 0.023$, $wR_{ref}(F) = 0.035$, $T = 296$ K.

Source of material

Crystals of phenylpiperazinium tetrachlorozincate were prepared by slow evaporation of an aqueous solution of phenylpiperazine, hydrochloride acid and zinc chloride (2:2:1). The obtained product was isolated by filtration and allowed to air-dry. The inorganic-organic hybrid compound crystals are stable for a long-time in normal conditions of temperature and humidity.

Experimental details

Due to the use of an incomplete data set of intensities, the expected accuracy of the bonding parameters could not be reached, e.g. $\sigma_{average}(N-C) = 0.004$ Å, $\sigma_{average}(C-C) = 0.005$ Å.

Discussion

The title inorganic-organic hybrid compound contains two basic components, the $[ZnCl_4]^{2-}$ anion and the organic cation (figure, top). The phenylpiperazine amine (PPIP) has two protonated ni-

trogen atoms. So, the structure can be described by $[ZnCl_4]$ units which form a hydrogen-bonded one-dimensional network with the phenylpiperazinium. The organic cation established both ionic interactions and strong hydrogen bonds with $[ZnCl_4]^{2-}$ anions ($N-H\cdots Cl$: $3.099(3)$ Å – $3.318(3)$ Å) to built infinite chains located at $y = 0$ and $\frac{1}{2}$ and spreading along the c direction (figure, bottom). The van der Waals contacts between these chains give rise to a three-dimensional network in the structure and add stability to this compound.

In the $[ZnCl_4]$ tetrahedra, the mean values of Zn–Cl bond lengths and Cl–Zn–Cl angles of 2.273 Å and 109.3° , respectively, are in agreement with those found in bis(2-amino-5-methylpyridinium) tetrachlorozincate (2.270 Å and 109.4° , respectively) [1]. The nearest Zn $\cdots$ Zn intra-chain distance is 6.086 Å, while that between adjacent chains is 7.427 Å. The atoms C5, C6, C7, C8, C9 and C10 of the phenyl ring of the title compound have a good planarity and they form a conjugated plane with average deviation of 0.0034 Å. The bond lengths of C5–C6, C5–C10, C6–C7, C7–C8, C8–C9 and C9–C10 are 1.353(3) Å, 1.365(4) Å, 1.390(5) Å, 1.358(5) Å, 1.370(5) Å and 1.385(5) Å, respectively, which are between single bond and double bond and agree with that in benzene [2]. Furthermore, the distances N1–C5, N1–C1, N1–C4, N2–C2, N2–C3, C1–C2 and C3–C4 [1.491(4) Å, 1.513(4) Å, 1.512(4) Å, 1.483(4) Å, 1.479(4) Å, 1.524(4) Å and 1.508(4) Å, respectively] indicate single bonds. In this compound, H6 and H7 attached to the N2 nitrogen atom and H1 attached to N1 nitrogen atom play an important role in forming the molecular association through hydrogen bonding. Here two chlorine atoms, Cl1 and Cl4, act as acceptors of these $N-H\cdots Cl$ bonds. The other two chlorine atoms, Cl2 and Cl3, do not participate in the hydrogen bonding network.

The deviation from the perfect tetrahedral arrangement around Zn(II) in the title compound can be explained by involving of the chlorine ions in hydrogen bonding. In this complex, only the Cl4 atoms form two hydrogen bonds, which reduce the fractional charge on the Cl4 atom and lead to an elongation of Zn–Cl4 bond by 0.06 Å compared to that of Zn–Cl1 bond. Since Cl2 and Cl3 atoms do not participate in the hydrogen bonding, the electrostatic repulsions between Cl2 and Cl3 atoms are more pronounced resulting in the opening up of the Cl2–Zn–Cl3 angle to $116.82(4)^\circ$ and in a comparatively larger deviation from the perfect tetrahedral arrangement around Zn(II). Similar features have been also observed in the structure of (benzotriazole)₂[CoCl₄] [3], where only two chlorine atoms are engaged in the hydrogen bonding network causing an elongation of the Co–Cl bonds by 0.06 Å and opening up the Cl–Co–Cl angle involving the other two non-hydrogen bonded chlorine atoms. Thus, in this latter compound, the hydrogen bonding network and the deviation from ideal tetrahedral arrangement are comparable to those of the title compound.

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Table 1. Data collection and handling.

Crystal:	colorless, parallelepipedic, size 0.20 × 0.30 × 0.90 mm
Wavelength:	Mo K α radiation (0.7107 Å)
μ :	23.71 cm ⁻¹
Diffraction, scan mode:	Enraf-Nonius MACH3, $\omega/2\theta$
$2\theta_{\max}$:	49.94°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	1885, 1004
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 897
$N(\text{param})_{\text{refined}}$:	154
Programs:	SIR92 [4], teXsan [5]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{iso}
H(1)	4e	-0.2814	-0.1058	-0.0701	0.032
H(2)	4e	-0.5097	-0.0884	-0.3294	0.031
H(3)	4e	-0.5182	-0.0339	-0.2015	0.032
H(4)	4e	-0.2473	-0.0087	-0.1677	0.032
H(5)	4e	-0.3459	0.0134	-0.3388	0.025
H(6)	4e	-0.2295	-0.0755	-0.4184	0.063
H(7)	4e	-0.0804	-0.0312	-0.3083	0.032
H(8)	4e	-0.0235	-0.0963	-0.1397	0.022
H(9)	4e	-0.0143	-0.1410	-0.2733	0.030
H(10)	4e	-0.3014	-0.1758	-0.3021	0.032
H(11)	4e	-0.1976	-0.1936	-0.1446	0.028
H(12)	4e	-0.4772	-0.2387	-0.1993	0.032
H(13)	4e	-0.7007	-0.2982	-0.1426	0.021
H(14)	4e	-0.8570	-0.2510	0.0159	0.041
H(15)	4e	-0.7772	-0.1448	0.1075	0.049
H(16)	4e	-0.5499	-0.0891	0.0370	0.016

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zn(1)	4e	-0.14176(3)	-0.11119(2)	0.29117(3)	0.0344(1)	0.0439(4)	0.0195(3)	0.0001(1)	0.0109(1)	-0.0000(2)
Cl(1)	4e	-0.38399(6)	-0.10851(3)	0.38281(8)	0.0327(2)	0.0714(8)	0.0270(6)	-0.0038(3)	0.0129(2)	-0.0066(4)
Cl(2)	4e	-0.12870(7)	-0.20110(4)	0.16264(7)	0.0520(3)	0.0408(7)	0.0352(6)	0.0013(3)	0.0167(3)	-0.0045(4)
Cl(3)	4e	0.10175(6)	-0.08720(4)	0.46918(7)	0.0330(2)	0.0562(7)	0.0219(5)	-0.0015(3)	0.0070(2)	0.0006(4)
Cl(4)	4e	-0.17835(6)	-0.02577(4)	0.12472(7)	0.0462(2)	0.0398(7)	0.0218(6)	-0.0057(3)	0.0051(3)	0.0034(4)
N(1)	4e	-0.3687(2)	-0.11762(9)	-0.1420(2)	0.0300(7)	0.029(2)	0.015(2)	-0.0029(8)	0.0103(7)	0.003(1)
N(2)	4e	-0.1655(2)	-0.0573(1)	-0.3214(2)	0.0356(7)	0.037(2)	0.022(2)	-0.0055(9)	0.0141(8)	0.001(1)
C(1)	4e	-0.4446(2)	-0.0626(1)	-0.2450(3)	0.0352(9)	0.024(2)	0.035(2)	0.003(1)	0.013(1)	0.007(2)
C(2)	4e	-0.2957(3)	-0.0182(1)	-0.2671(3)	0.0454(9)	0.044(3)	0.019(2)	0.007(1)	0.019(1)	0.009(2)
C(3)	4e	-0.0944(3)	-0.1136(1)	-0.2271(3)	0.0326(8)	0.047(3)	0.028(2)	0.005(1)	0.015(1)	0.002(2)
C(4)	4e	-0.2434(2)	-0.1569(1)	-0.2069(3)	0.0394(9)	0.022(2)	0.022(2)	0.005(1)	0.0158(9)	-0.007(2)
C(5)	4e	-0.5095(2)	-0.1575(1)	-0.1017(2)	0.0314(8)	0.022(3)	0.015(2)	-0.004(1)	0.0106(9)	-0.002(2)
C(6)	4e	-0.5543(3)	-0.2181(2)	-0.1559(3)	0.048(1)	0.032(3)	0.044(2)	-0.010(1)	0.021(1)	-0.009(2)
C(7)	4e	-0.6839(3)	-0.2524(1)	-0.1092(3)	0.061(1)	0.037(3)	0.047(3)	-0.024(1)	0.027(1)	-0.027(2)
C(8)	4e	-0.7651(3)	-0.2257(1)	-0.0130(3)	0.043(1)	0.026(3)	0.038(2)	-0.008(1)	0.015(1)	0.001(2)
C(9)	4e	-0.7195(2)	-0.1639(2)	0.0392(3)	0.0385(9)	0.042(3)	0.030(2)	0.006(1)	0.018(1)	0.003(2)
C(10)	4e	-0.5901(2)	-0.1293(1)	-0.0059(3)	0.0380(9)	0.030(2)	0.026(2)	-0.005(1)	0.011(1)	-0.012(2)

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