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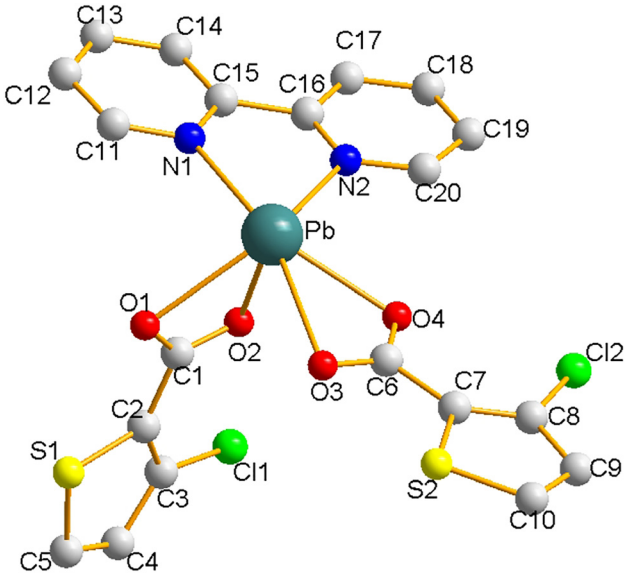
The crystal structure of (3-chlorothiophene-2-carboxylato-κ^2O, O')-(2,2′-dipyridyl-κ^2N,N') lead(II), $C_{20}H_{12}Cl_2N_2O_4S_2Pb$



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Abstract

$C_{20}H_{12}Cl_2N_2O_4S_2Pb$, monoclinic, $P2_1/c$ (no. 14), a = 13.2710(4) Å, b = 16.7810(4) Å, c = 9.6857(2) Å, β = 96.5550(1)°, V = 2142.91(9) Å^3, Z = 4, $R_{gt}(F)$ = 0.0314, $wR_{ref}(F^2)$ = 0.0807, T = 150.0 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.

1 Source of materials

3-Chlorothiophene-2-carboxylic acid (2.0 mmol) was dissolved in 20 mL of anhydrous methanol. $Pb(CH_3COO)_2$ (1.0 mmol) dissolved in 10 mL of anhydrous methanol was added dropwise to the above 3-chlorothiophene-2-carboxylic acid solution and stirred for 2 h at 50 °C. Then 2,2′-dipyridyl (1.0 mmol) was dissolved in 10 mL of anhydrous methanol and added dropwise to the above solution and stirred for 3 h at 50 °C cooled and filtered. The filtrate was left for slow evaporation at room temperature. The yellow block crystals were formed 14 days later. Yield: 41.7 %. Anal. Calcd. for $C_{20}H_{12}Cl_2N_2O_4S_2Pb$: C, 34.98; H, 1.76; N, 4.08; S, 9.34; found: C, 34.87; H, 1.72; N, 4.10; S, 9.33.

Table 1: Data collection and handling.

Crystal:	Yellow block
Size	0.20 × 0.20 × 0.20 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	8.35 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	26.4°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	50608, 4394, 0.053
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3762
$N(param)_{refined}$:	280
Programs:	Bruker,[1] Olex2[2]

2 Experimental details

Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on parent atoms.

3 Comment

In the last decades, the application of metal complexes for the treatment of cancer were extensively explored and consequently, metal complexes were recognized as promising anticancer agents.[3,4] The chemical structures of thiophene and pyridine with heterocyclic compounds have antibacterial, anticancer and anti-inflammatory effects.[5,6] As a part of our current research interest on the biological activity of metal complexes, we report herein a new ternary lead metal complex constructed by 3-chlorothiophene-2-carboxylate and 2,2′-dipyridyl ligands. Single crystal

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Pb1	0.17230 (2)	0.56041 (2)	0.51915 (2)	0.03088 (8)
Cl1	0.33027 (12)	0.27700 (12)	0.7301 (3)	0.0793 (6)
Cl2	0.47136 (11)	0.66114 (10)	0.93610 (17)	0.0522 (4)
S1	0.01328 (11)	0.29835 (10)	0.72220 (17)	0.0509 (4)
S2	0.17355 (12)	0.66688 (10)	1.05059 (16)	0.0486 (4)
O1	0.0592 (3)	0.4360 (2)	0.5632 (4)	0.0406 (8)
O2	0.2269 (3)	0.4309 (2)	0.5924 (4)	0.0362 (8)
O3	0.1409 (3)	0.5887 (3)	0.7873 (4)	0.0539 (11)
O4	0.2984 (3)	0.5880 (2)	0.7293 (4)	0.0414 (8)
N1	0.1745 (3)	0.4958 (2)	0.2791 (4)	0.0338 (9)
N2	0.3416 (3)	0.5618 (2)	0.4164 (5)	0.0337 (9)
C1	0.1406 (4)	0.4015 (3)	0.6077 (5)	0.0322 (10)
C2	0.1335 (4)	0.3265 (3)	0.6851 (5)	0.0343 (10)
C3	0.2028 (4)	0.2733 (3)	0.7451 (6)	0.0438 (13)
C4	0.1622 (5)	0.2126 (3)	0.8223 (6)	0.0464 (13)
H4	0.201417	0.171859	0.870646	0.056*
C5	0.0614 (5)	0.2194 (4)	0.8193 (7)	0.0541 (15)
H5	0.021047	0.184004	0.866298	0.065*
C6	0.2332 (4)	0.6037 (3)	0.8113 (5)	0.0364 (11)
C7	0.2673 (4)	0.6444 (3)	0.9454 (5)	0.0379 (11)
C8	0.3586 (5)	0.6702 (3)	1.0070 (6)	0.0425 (12)
C9	0.3557 (5)	0.7075 (3)	1.1374 (6)	0.0485 (14)
H9	0.413280	0.728313	1.192903	0.058*
C10	0.2593 (5)	0.7094 (4)	1.1728 (6)	0.0529 (15)
H10	0.241753	0.732140	1.256658	0.063*
C11	0.0870 (4)	0.4697 (3)	0.2101 (6)	0.0407 (12)
H11	0.025804	0.476602	0.250868	0.049*
C12	0.0834 (5)	0.4331 (4)	0.0818 (6)	0.0487 (14)
H12	0.020910	0.414407	0.035509	0.058*
C13	0.1717 (5)	0.4242 (5)	0.0228 (6)	0.0548 (17)
H13	0.170762	0.399720	−0.065759	0.066*
C14	0.2628 (5)	0.4510 (4)	0.0926 (6)	0.0474 (14)
H14	0.324682	0.444037	0.053513	0.057*
C15	0.2617 (4)	0.4882 (3)	0.2203 (5)	0.0347 (11)
C16	0.3541 (4)	0.5233 (3)	0.2980 (5)	0.0336 (10)
C17	0.4482 (4)	0.5197 (3)	0.2491 (6)	0.0383 (11)
H17	0.455939	0.491201	0.166209	0.046*
C18	0.5308 (4)	0.5576 (3)	0.3206 (7)	0.0442 (13)
H18	0.595542	0.554944	0.287771	0.053*
C19	0.5182 (4)	0.5994 (3)	0.4400 (6)	0.0427 (13)
H19	0.572956	0.627277	0.490065	0.051*
C20	0.4217 (4)	0.5989 (3)	0.4843 (5)	0.0361 (11)
H20	0.412326	0.626589	0.567521	0.043*

X-ray diffraction analysis demonstrates that the asymmetric unit of the title structure contains one lead(II), two 3-chlorothiophene-2-carboxylate ligands and one 2,2′-dipyridyl ligand. The bond distances of Pb–N are 2.560(4) and 2.568 (4) Å, bond lengths of Pb–O are 2.374(3)–2.719(4) Å, respectively, which are similar with refs.[7,8] The Pb (II) is six coordinated by four oxygen and two nitrogen atoms from the 3-chlorothiophene-2-carboxylic acid ligands and one 2,2′-dipyridyl. There are two four-membered chelate rings (Pb–O(1)–C(1)–O(2), Pb(1)–O(3)–C(6)–O(4)) and one five-membered chelate ring (Pb–N(1)–C(15)–C(16)–N(2)). But the geometry of the complex is different from octahedron geometry, which forms an umbrella-like geometry in which Pb–O(2) bond serves as the umbrella handle.[9,10]

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References

1. Bruker. *APEX2*, *SAINT* and *SADABS*; Bruker AXS Inc.: Madison,: Wisconsin, USA, 2004.
2. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
3. Takasaki, S.; Takamizawa, S. Reversible Crystal Deformation of Asingle-Crystal Host of Copper (II) 1-Naphthoate-Pyrazine through Crystal Phase Transition Induced by Methanol Vapor Sorption. *Chem. Commun.* **2015**, *51*, 5024–5027.
4. Yarnell, A.; Oh, S.; Reinberg, D.; Lippard, S. Interaction of FACT, SSRP1, and the High Mobility Group (HMG) Domain of SSRP1 with DNA Damaged by the Anticancer Drug Cisplatin. *J. Biol. Chem.* **2001**, *276*, 25736–25741.
5. Wei, M.; Peng, X.; Xing, L.; Dai, Y.; Huang, R.; Geng, M.; Zhang, A.; Ai, J.; Song, Z. Design, Synthesis and Biological Evaluation of a Series of Novel 2-Benzamide-4-(6-Oxy-n-Methyl-1-Naphthamide)-Pyridine Derivatives as Potent Fibroblast Growth Factor Receptor (fgfr) Inhibitors. *Eur. J. Med. Chem.* **2018**, *154*, 9–28.
6. Ndagi, U.; Mhlongo, N.; Soliman, M. E. Metal Complexes in Cancer Therapy – an Update from Drug Design Perspective. *Drug Des. Dev. Ther.* **2017**, *11*, 599–616.
7. Kowalik, M.; Masternak, J.; Kazimierczuk, K.; Kupcewicz, B.; Khavryuchenko, O. V.; Barszcz, B. Exploring Thiophene-2-Acetate and Thiophene-3-Acetate Binding Modes towards the Molecular and Supramolecular Structures and Photoluminescence Properties of Pb(II) Polymers. *CrystEngComm* **2020**, *22*, 7025–7035.
8. Deng, Z.; Li, J.; Hou, X.; Luo, N.; Zhu, X. The Crystal Structure of di-μ-1-Naphthylacetato-$\kappa^3O,O':O$; $\kappa^3O:O,O'$-bis[(1-Naphthylacetato-

κ^2O,O')(2,2′-bipyridine-κ^2N,N')Lead(II)] Monohydrate, $C_{68}H_{54}N_4O_9Pb_2$. *Z. Kristallogr. N. Cryst. Struct.* **2023**, *238*, 483–485.

9. Guo, F.; Su, C.; Fan, Y.; Fu, W. Two Pb(II) Coordination Complexes Based on 5-halonicotinate (Cl or Br): Structural Diversities and Sensing Performance. *J. Solid State Chem.* **2019**, *277*, 83–92.
10. Zhang, Z.; Bi, C.; Fan, Y.; Yan, X.; Zhang, P.; Huang, G. Synthesis, Crystal Structures, Luminescent Properties, Theoretical Calculation, and DNA Interaction of the Cadmium(II) and Lead(II) Complexes with o-Aminobenzoic Acid and 1,10-Phenanthroline1. *Russ. J. Coord. Chem.* **2015**, *41*, 274–284.