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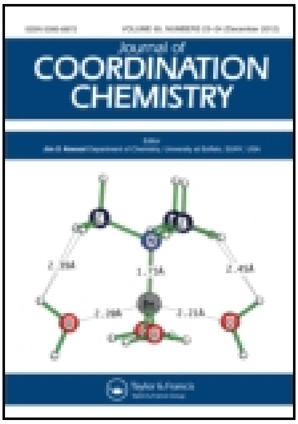

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Syntheses, characterization, and supramolecular architectures of two lead(II) complexes of 8-quinolinol

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Syntheses, characterization, and supramolecular architectures of two lead(II) complexes of 8-quinolinol

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Two Pb(II) complexes with 8-quinolinol (8-Quin), 5-chloro thiophene-2-carboxylic acid, and (5-CTPC)/5-bromo thiophene-2-carboxylic acid (5-BTPC) have been synthesized and characterized by IR, ^{13}C NMR, and solid state photoluminescence spectra. The structures of $[Pb(8\text{-}Quin)_4](5\text{-}CTPC)_2$ (**1**) and $[Pb(8\text{-}Quin)_2(8\text{-}Quio)](5\text{-}BTPC)$ (**2**) [(8-Quio) = 8-quinolinolate] have been confirmed by X-ray crystallography. Both complexes crystallize in the triclinic crystal system with a space group $P\bar{1}$. In **1**, Pb(II) is eight coordinate by four bidentate 8-quinolinol groups, while in **2** it is six coordinate by two bidentate 8-quinolinol groups and one bidentate 8-quinolinolate group. This leads to square antiprismatic and pentagonal pyramidal geometries around Pb(II) in **1** and **2**, respectively. Two of the 5-CTPC ligands in **1** and a 5-BTPC in **2** are involved in strong O–H···O hydrogen bonding in the lattice. Cl···π interactions are found in **1**. The crystal structures are stabilized by weak C–H···O and π–π stacking interactions.

Keywords: Thiophene 2-carboxylic acid; Pb(II); Single-crystal diffraction studies; π–π Stacking interaction; Fluorescence

1. Introduction

Construction of organic–inorganic hybrid materials is of interest for interesting framework structures [1–9] and a variety of applications [1, 10–12]. Coordination complexes based on s, d, and even f block metal ions have been studied [13–15], but main group elements show unique coordination modes as well as electronic properties compared to d-block elements; complexes of nontransition metals have diverse structures. Valence s and p electrons play a major role in molecular structure. The metals also show applications in photovoltaic conversion, fluorescent sensors, and electroluminescent devices [16].

Lead is highly toxic, occurring in both biological systems and natural environment. As an important p-block element, the coordination chemistry of Pb(II) complexes is of interest. Pb(II) displays interesting structural features as a result of a large radius, coordination numbers from 2 to 10 and potentially a stereochemically active lone pair [17–21]. Pb(II) exhibits inert pair effect and its complexes show the stereochemical

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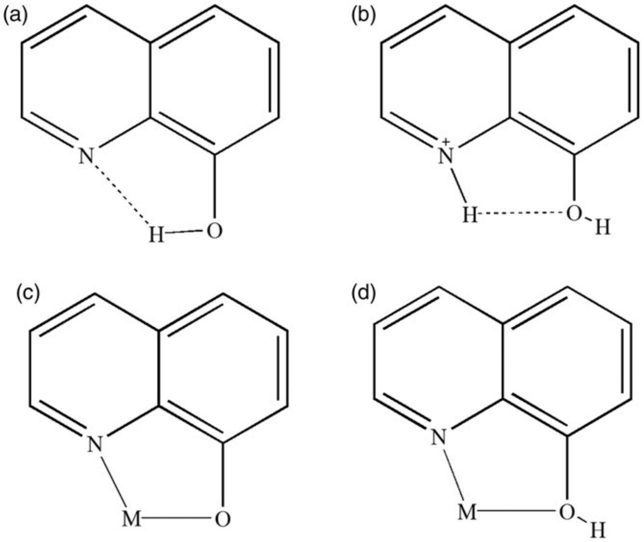
activity of the valence shell electron lone pair [17, 21–24], making Pb(II) complexes interesting [25–27].

8-Hydroxyquinoline (8-quinolinol, oxine) and derivatives are good complexing agents with metal ions [28–30], acting as both neutral and anionic ligands (scheme 1c, 1d). In some structures the protonated hydrogen atom at N1 of the 8-hydroxyquinolinium mimics the role of metal centre, producing similar patterns (scheme 1) [31]. They are used as reagents in the extraction of metals in analytical chemistry and for metal preparation in hydro metallurgy [32]. Some of its metal complexes with copper(II), zinc(II), or nickel(II) have remarkable antibacterial and antifungal properties [33, 34]. Its Bi(III) complex shows antitumor activity against leukemia [35]. Various remarkable structural features of metal complexes of oxine and derivatives have been reported by our group [36–39]. In continuation of our previous work, we now investigate the interactions of lead(II) ion with 8-quinolinol using 5-CTPC and 5-BTPC as ancillary ligands (scheme 1). Furthermore, we discuss the influence of two different carboxylates on the final crystal structures of **1** and **2**. The photoluminescence properties of **1** and **2** are also reported.

2. Experimental

2.1. *Materials and methods*

Commercial starting materials were used without purification. 8-Hydroxyquinoline (Loba Chemie), 5-chloro thiophene 2-carboxylic acid (Hoechst Aktiengesellschaft), methanol (Qualigens), 5-bromo thiophene 2-carboxylic acid (Aldrich), and



Scheme 1. (a) and (b) Schematic representation of hydrogen bonding patterns in neutral and protonated 8-quinoninol. (c) and (d) Schematic representation of coordination mode of 8-quinolinolate and 8-quinolinol with metal.

$Pb(CH_3COO)_2 \cdot 3H_2O$ (Reidel) were used. IR spectra of the complex from 400 to 4000 cm^{-1} were recorded as pressed disks (1% by weight in KBr) on a Shimadzu FT IR spectrophotometer and a Perkin Elmer. ^{1}H-NMR and ^{13}C-NMR spectra were recorded with a Bruker spectrometer at 400 MHz in [D6] DMSO. The fluorescence properties were studied in the solid state on a HITACHI spectrofluorimeter at room temperature. Both the excitation slit and emission slit were 5 nm.

2.2. *Preparation of [Pb(8-Quin)$_4$](5-CTPC)$_2$ (1)*

A methanol solution of 8-hydroxyquinoline (0.0543 g) was added into an aqueous solution of lead(II) acetate (0.1093 g). The mixture was stirred and heated for 30 min. To this mixture, a methanol solution of 5-CTPC (0.0443 g) was added to give a clear yellow solution. The resulting solution was allowed to stand in air at room temperature for 2 weeks. Yellow single crystals suitable for X-ray diffraction were obtained (yield = 66% based on Pb). IR selected bands (cm^{-1}): 3563(w), 3104(m), 2929(m), 1565(s), 1539(s), 1433(w), 1433(s), 1389(s), 1314(m), 1205(m), 1117(m), 1056(m), 997(m), 765(s), 673(m), 519(m), 469(m). ^{13}C NMR (DMSO): $\delta = 113.10$, 115.20, 121.56, 127.52, 128.39, 129.38, 129.86, 131.15, 136.79, 140.36, 143.15, 147.26, 165.25. The schematic representation of the complex is given in scheme 2(a).

2.3. *Preparation of [Pb(8-Quin)$_4$](5-BTPC)$_2$ (2)*

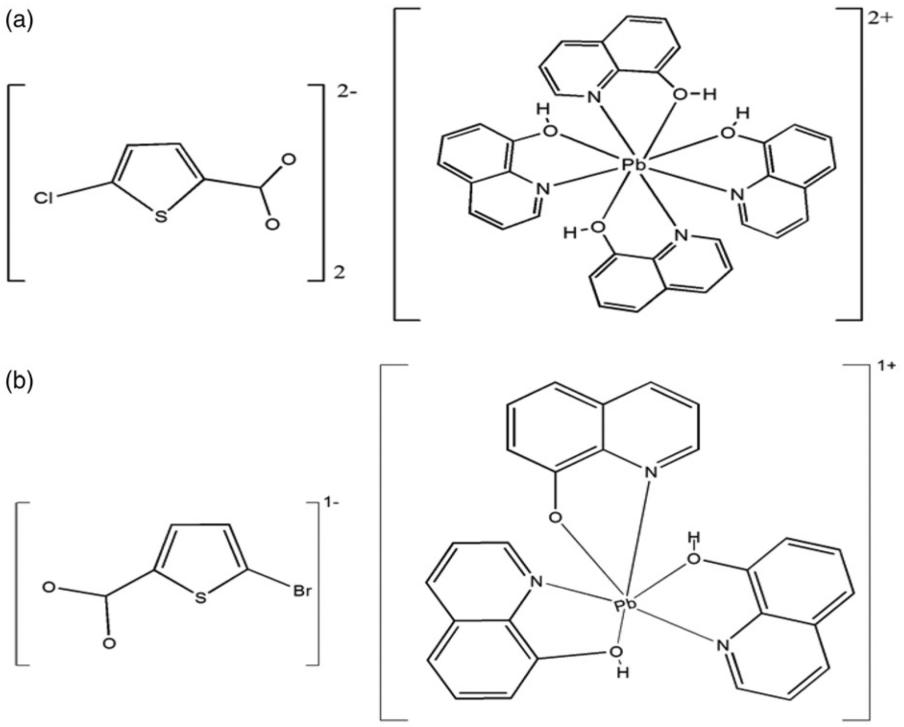
The reaction conditions and procedures for the preparation of **2** were the same as that of **1**, except 5-BTPC was used in the place of 5-CTPC (yield = 52% based on Pb). IR selected bands (cm^{-1}): 3417(w), 2929(m), 1566(s), 1494(s), 1457(s), 1420(s), 1371(s), 1316(s), 1273(s), 1101(s), 821(s), 728(s) cm^{-1}. ^{13}C NMR (DMSO): $\delta = 114.03$, 114.40, 121.34, 129.11, 129.31, 130.75, 137.34, 146.37, 147.54. The schematic representation of the complex is given in scheme 2(b).

2.4. *Characterization of the complexes*

IR spectra: Assignments of selected characteristic IR bands (4000–400 cm^{-1}) of the two Pb(II) complexes have been carried out. Spectra of **1** and **2** show the carboxyl stretching vibrations of 5-TPC. The asymmetric and symmetric stretches $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ were observed at 1565 and 1389 cm^{-1}, 1566 and 1371 cm^{-1} for **1** and **2**, respectively. The $\Delta = \nu_{as}(COO^-) - \nu_s(COO^-) = 176$ and 195 cm^{-1} for **1** and **2**, respectively, only slightly higher than the expected values for ionic carboxylate (170 cm^{-1}) [40].

2.5. *Crystal structure determinations*

Intensity data sets were collected at room temperature on a BRUKER SMART APEXII CCD [41] area-detector diffractometer equipped with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The data were reduced using SAINT [41] and empirical absorption corrections were done using SADABS [41]. The structures were solved by direct methods using SHELXS-97 [42] and subsequent Fourier analyses,



Scheme 2. Schematic representation of **1** and **2**.

refined anisotropically by full-matrix least-squares method using SHELXL-97 [42] within the WINGX suite of software, based on F^2 with all reflections. All hydrogen atoms on carbon were positioned geometrically and refined by a riding model with Uiso 1.2 times that of carbon. All non H atoms were refined anisotropically. Hydrogen atoms of the hydroxy groups of 8-Quin were located in difference Fourier maps. The molecular structures were drawn using ORTEP-III [43] and POV-ray [44]. Crystal data and selected parameters are summarized in tables 1 and 2, respectively. The crystals remained stable throughout data collection.

3. Results and discussion

3.1. *Geometry around Pb(II) atom*

The lone pair of electrons has a great influence on the structure of the complexes [17, 23]. The coordination numbers of lead in **1** and **2** are eight and six, respectively, displaying square antiprismatic and pentagonal pyramidal geometries. In **1** each lead is surrounded by four nitrogen atoms and four oxygen atoms from four neutral 8-Quin. Both upper and lower prisms contain the alternative arrangement of nitrogen and oxygen atoms(figure 1a). In **2** the axial position of the pentagonal pyramid is occupied by N1 from the 8-Quio anion (figure 1b). The arrangement of 8-Quin around Pb(II) in **1**

Table 1. Crystal data and structure refinement information.

	1	**2**
Empirical formula	$C_{36}H_{28}N_4O_4Pb$, $2(C_5H_2ClO_2S)$	$C_{27}H_{20}N_3O_3Pb$, $C_5H_2BrO_2S$
Formula weight	1111.00	847.70
Temperature (K)	296	296
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions (Å, °)		
a	10.8929(1)	11.727(5)
b	11.5760(1)	11.821(5)
c	17.8963(2)	12.256(5)
α	96.141(1)	69.866(5)
β	99.217(1)	75.686(5)
γ	95.774(1)	71.666(5)
Volume (Å^3), Z	2198.74(4), 2	1495.7(11), 2
Calculated density (g cm^{-3})	1.678	1.882
Absorption coefficient (mm^{-1})	4.112	7.092
$F(000)$	1096	816
Crystal size (mm^3)	0.04 × 0.04 × 0.05	0.08 × 0.09 × 0.09
Number of reflections collected	8181	9641
Number of restraints	0	0
Goodness-of-fit on F^2	1.03	1.04
Final R_1 index $[I > 2\sigma(I)]$	0.0308	0.0329
wR_2 (all data)	0.0679	0.0790
Largest difference peak and hole (e Å^{-3})	−0.40 and 0.53	−1.23 and 1.18

$R_1 = \sum(||F_o|-|F_c||)/\sum|F_o|$; $wR_2 = [\sum w(|F_o|-|F_c|^2)^2] / \sum w(|F_o|^2)]^{1/2}$.

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

Complex **1**		Complex **1**		Complex **2**	
Pb1–O1	2.639(3)	O1–Pb1–O2	125.05(10)	O1–Pb1–O2	133.73(8)
Pb1–O2	2.568(3)	O1–Pb1–O3	78.11(10)	O1–Pb1–O3	129.01(8)
Pb1–O3	2.606(3)	O1–Pb1–O4	133.10(10)	O1–Pb1–N1	70.64(11)
Pb1–O4	2.668(3)	O1–Pb1–N1	59.70(10)	O1–Pb1–N2	84.05(10)
Pb1–N1	2.779(3)	O1–Pb1–N2	82.04(11)	O1–Pb1–N3	78.41(10)
Pb1–N2	2.650(3)	O1–Pb1–N3	139.53(10)	O2–Pb1–O3	72.35(7)
Pb1–N3	2.647(3)	O1–Pb1–N4	87.22(10)	O2–Pb1–N1	75.43(10)
Pb1–N4	2.716(3)	O2–Pb1–O3	124.95(11)	O2–Pb1–N2	60.14(9)
		O2–Pb1–O4	78.37(10)	O2–Pb1–N3	129.31(9)
Complex **2**		O2–Pb1–N1	75.62(10)	O3–Pb1–N1	79.90(10)
Pb1–O1	2.271(3)	O2–Pb1–N2	62.51(10)	O3–Pb1–N2	131.86(9)
Pb1–O2	2.753(3)	O2–Pb1–N3	79.99(10)	O3–Pb1–N3	58.15(9)
Pb1–O3	2.824(3)	O2–Pb1–N4	138.85(10)	N1–Pb1–N2	81.22(11)
Pb1–N1	2.435(4)	O3–Pb1–O4	124.67(10)	N1–Pb1–N3	85.40(11)
Pb1–N2	2.643(3)	O3–Pb1–N1	135.40(10)	N2–Pb1–N3	160.70(11)
Pb1–N3	2.701(4)	O3–Pb1–N2	75.18(10)	O4–C28–O5	125.5(5)
		O3–Pb1–N3	61.57(10)		
		O3–Pb1–N4	82.53(10)		
		O4–Pb1–N1	96.36(10)		
		O4–Pb1–N2	139.38(10)		
		O4–Pb1–N3	78.20(10)		
		O4–Pb1–N4	60.48(10)		
		O7–C42–O8	126.9(5)		
		O5–C37–O6	126.4(4)		

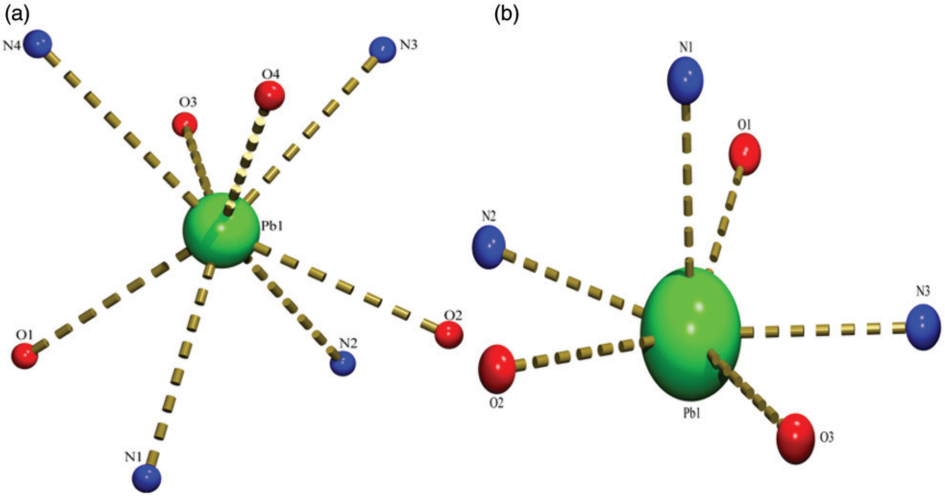


Figure 1. Representation of the geometries and environment around Pb(II) in **1** and **2**, respectively.

does not show a gap or hole in the coordination geometry, indicating that the lone pair of electrons on lead(II) is inactive in this complex. The coordination geometry of **2** shows a gap around Pb(II), occupied possibly by a stereoactive lone pair of electrons giving hemidirected coordination. In **1** the coordination geometry is holo directed and the difference between the Pb–O and Pb–N is relatively small. In **2**, which is hemidirected, there is a large difference between Pb–O and Pb–N distances, indicating an active lone pair.

3.2. *Crystal structure description of [Pb(8-Quin)$_4$](5-CTPC)$_2$] (1)*

The asymmetric unit of **1** consists of four neutral 8-Quin coordinated to lead. In addition, two 5-CTPC anions are ligands of crystallization. Four O–H···O hydrogen bonds (table 3) are found between hydroxyl groups of 8-Quin and 5-CTPC (figure 2). Each pair of O–H···O hydrogen bonds with two 8-hydroxyquinoline and a 5-CTPC lie in the same plane (figure 2). Also there are weak C–H···O hydrogen bonds between the hydroxyl oxygen atoms of the 8-hydroxyquinolines and carboxylate oxygens. π–π Stacking interactions can be found between the five-membered rings of the thiophene carboxylic acid [S2, C43, C44, C45, C46] and nitrogen-containing six-membered rings of 8-Quin [N1, C1, C2, C3, C8, C9] (figure 3). Such interactions are also found between two six-membered rings of 8-Quin (figure 3).

C–O bonds of 8-quinoninol are slightly longer than in other 8-quinolinato metal complexes ($\sim$1.32 Å) and shorter than the normal single bond in ether and alcohols ($>$1.4 Å). The C–O bond lengths of coordinated 8-quinoninol ligands lie in the range of 1.36 Å. The Pb–N and the Pb–O distances of [Pb(8-Quin)$_4$](5-CTPC)$_2$ lies in the ranges of 2.7 Å and 2.6 Å, respectively, which is slightly higher than similar complexes [45–51]. The O–C– bond angles of the carboxylates are O5–C38–O6 = 126.3(4)°, O7–C43–O8 = 126.8(5)°, while that of aromatic carboxylates lie at the lattice 122–123°. The four chelate rings, Pb1/O1/C7/C9/N1, Pb1/O2/C16/C18/N2, Pb1/O3/C25/C27/N3, and

Table 3. Hydrogen bonding parameters (Å, °).

D–H···A	D–H	H···A	D···A	D–H···A
Complex **1**				
O1–H1A···O8	0.75(5)	1.81(5)	2.545(5)	168(6)
O2–H2A···O5	0.75(4)	1.71(4)	2.453(5)	171(5)
O3–H3A···O7	0.91(4)	1.60(5)	2.498(5)	175(4)
O4–H4A···O6	0.80(3)	1.77(3)	2.564(5)	170(5)
C15–H15···O5	0.9300	2.5600	3.130(5)	120.00
C24–H24···O7	0.9300	2.5800	3.197(6)	124.00
C33–H33···O6	0.9300	2.5500	3.201(5)	127.00
Complex **2**				
O2–H1A···O4	0.81(4)	1.71(4)	2.519(5)	177(3)
O3–H2A···O5	0.80(3)	1.79(3)	2.583(4)	169(4)
C1–H1···O2	0.9300	2.5700	3.138(6)	120.00
C15–H15···O4	0.9300	2.5100	3.149(6)	126.00
C19–H19···O1	0.9300	2.5100	3.149(5)	126.00

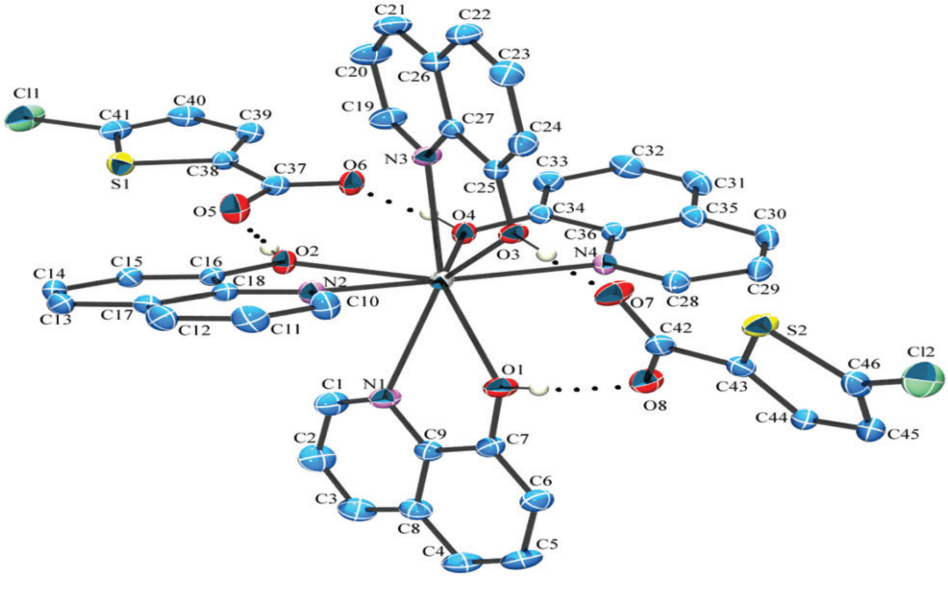


Figure 2. ORTEP of **1** showing the atom-numbering scheme and hydrogen bonding in coordinated ligands. Displacement ellipsoids are drawn at the 50% probability level for all non hydrogen atoms; hydroxy hydrogen atoms involved in hydrogen bonding are shown as small spheres of arbitrary radii. All other hydrogen atoms are omitted for clarity.

Pb1/O4/C34/C36/N4, make dihedral angles of 84.27(15)°, 83.10(15)°, 88.69(15)°, and 74.22(15)°, respectively, with each other.

The mean chelate angles Pb–O–C, Pb–N–C and the mean bite angle O–Pb–N are close to reported metal complexes of 8-hydroxyquinoline (table 2). A Cl···π interaction is found between Cl1 of the five-membered thiophene ring involving C41, C40, C39, C38, S1 and the six-membered N-hetero ring of 8-Quin involving N4^{i}, C28^{i}, C29^{i},

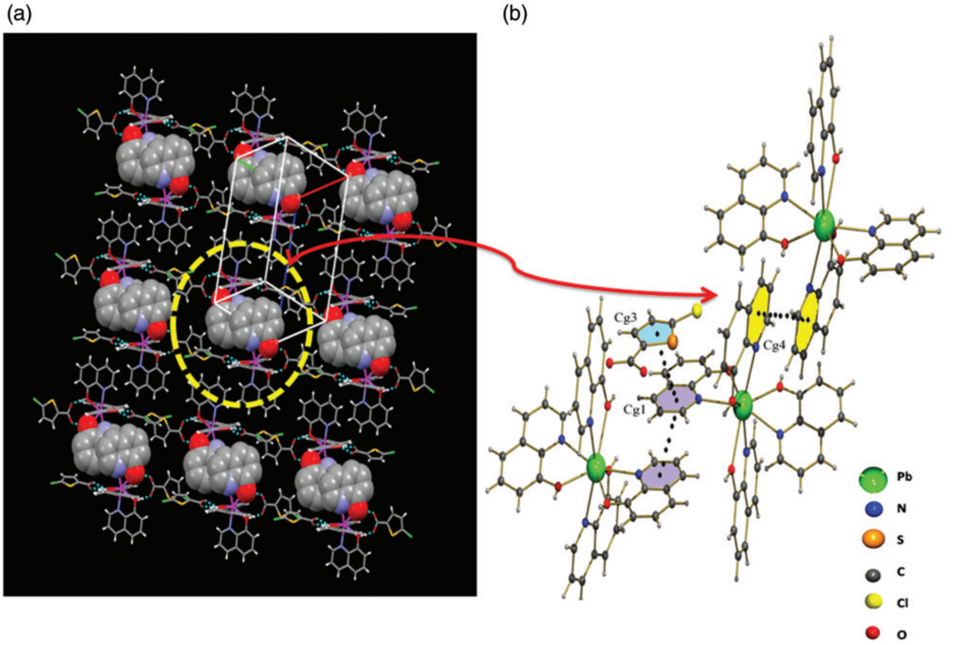


Figure 3. (a) A view of the π–π stacking interactions between two quinoline rings shown as a space-filled model. (b) Packing diagram showing the π–π stacking interactions as dashed lines in **1**.

C30^{i}, C35^{i}, C36^{i} [symmetry code i: $x,-1+y,z$] (figure 4b). Each Pb(II) is connected by the Cl$\cdots\pi$ interaction forming a chain which extends along the *b*-axis. Two of these adjacent chains are interlinked by the C4–H4$\cdots$Cg2^{ii} [symmetry code ii: $1-x,1-y,1-z$] (figure 4a). Cg2 = [C13, C14, C15, C16, C18, C17].

3.3. *Crystal structure description of [Pb(8-Quin)$_2$(8-Quio)](5-BTPC)] (2)*

The asymmetric unit of **2** consists of two neutral 8-Quin and a 8-Quio anions coordinated to lead. The two neutral 8-Quin ligands lie on the same plane while 8-Quio anion lies perpendicular to the plane containing the neutral 8-Quin. The Pb–N and the Pb–O distances of **2** depend on 8-Quin and 8-Quio anion with Pb–N and the Pb–O distances of the 8-Quio anion less than that of the neutral 8-Quin (table 2).

Similar to **1** where two 5-CTPC anions have O–H$\cdots$O bonding interactions, in **2** a 5-BTPC anion is present as a ligand of crystallization that exhibits O–H$\cdots$O hydrogen bonds (table 3) with the hydroxyl groups of neutral 8-Quin (figure 5). The O4–C28–O5 bond angle of carboxylate is 125.5(5)°. There are weak C–H$\cdots$O hydrogen bonds between hydroxyl oxygen atoms of the 8-hydroxyquinolines and carboxylate oxygen atoms (table 3).

Two symmetry-related Pb(II) monomers are connected by π–π stacking interactions between 8-Quin (Cg1 $\rightarrow$ Cg2^{i} and Cg2 $\rightarrow$ Cg4^{i} [symmetry code i = $2-x,1-y,2-z$]). The Pb$\cdots$Pb separation is 4.086 Å and these monomeric units are further connected by π–π stacking interactions Cg1 $\rightarrow$ Cg1^{ii} and C–H$\cdots$Cg3^{ii} [symmetry code ii = $2-x$, $1-y$, $1-z$]. [Cg1 = N2, C10, C11, C12, C17, C18; Cg2 = C22, C23, C24, C25, C27, C26;

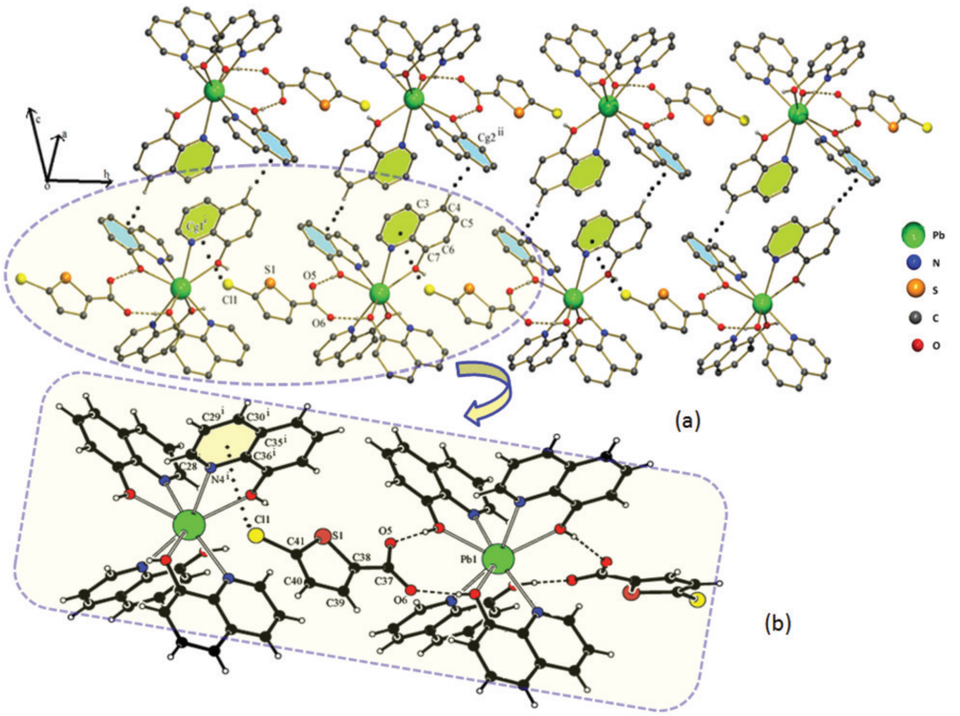


Figure 4. (a) The Pb(II) monomeric units connected by the Cl···π interaction forming chains which extend along the *b*-axis. (b) A projected view of the packing diagram showing the Cl···π interaction as bold dotted lines [symmetry code: i: *x*,−1 + *y*,*z*].

Cg3 = C4, C5, C6, C7, C9, C8; Cg4 = C13, C14, C15, C16, C18, C17]. These π–π stacking and C–H···π interactions form chains of monomeric units along the *c*-axis (figure 6).

3.4. *Luminescent properties*

Photoluminescence of main group metal complexes are less investigated than transition and lanthanide-metal complexes [52–54]. Luminescent properties of **1** and **2** have been investigated in the solid state at room temperature. Compounds **1** and **2** exhibit intense and broad emission bands with maxima at *ca* 543 and 544 nm upon excitation at 456 and 457 nm (Supplementary material); emission spectra of **1** and **2** are similar. According to previous reports, this emission band could be assigned to ligand-to-metal charge transfer (LMCT) [55, 56]. The observation indicates that **1** and **2** may be used as candidates for a new class of photoactive materials.

4. Conclusions

We prepared and studied the first lead complex with 8-Quin and thiophene carboxylic acid. In contrast to previously reported Pb(II) coordination complexes which contain quinolinate anions, Pb(8-Quin)$_4$](5-CTPC)$_2$ (**1**) and [Pb(8-Quin)$_2$(8-Quio)](5-BTPC) (**2**)

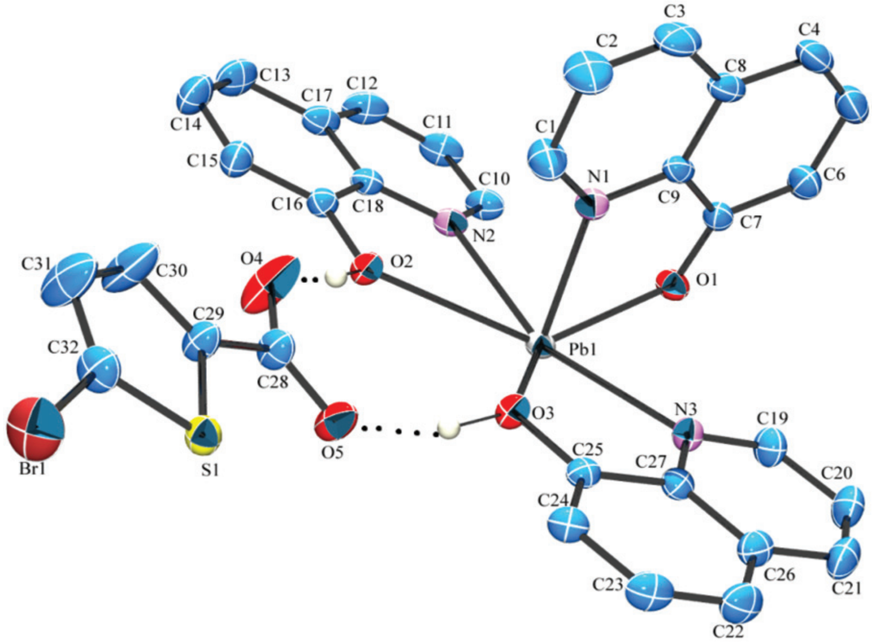


Figure 5. ORTEP of **2** showing the atom-numbering scheme and hydrogen bonding in coordinated ligands. Displacement ellipsoids are drawn at the 50% probability level for all non hydrogen atoms; hydroxy H involved in hydrogen bonding are shown as small spheres of arbitrary radii. All other hydrogen atoms are omitted for clarity.

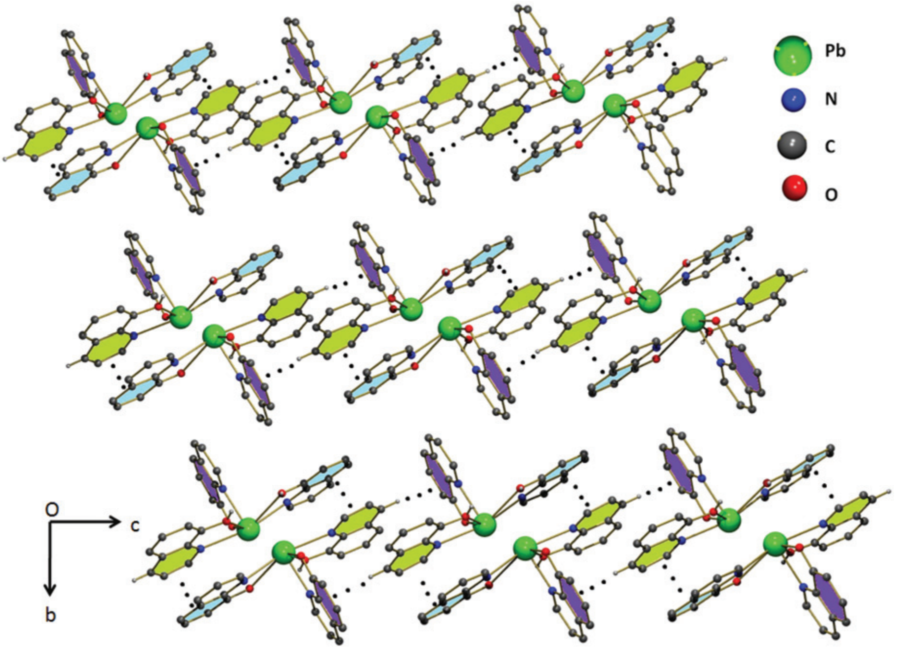


Figure 6. A view of the π–π stacking interactions along the *a*-axis; hydrogen atoms and 5-BTPC are omitted for clarity.

show the less-commonly occurring neutral coordinated 8-Quin. Complexes **1** and **2** are structurally different, illustrating the influence of halo substituent in the thiophene carboxylates. There are Cl–π interactions in **1** and no such Br–π interactions in **2**. The carboxylates allow the formation of O–H···O hydrogen bonds. Solid state emission spectra of **1** and **2** have emission peaks at 543 and 544 nm upon excitation at 456 and 457 nm.

Supplementary material

CCDC 874816 and CCDC 874815 contain the supplementary crystallographic data for **1** and **2**, respectively, and can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 IEZ, UK; Fax: (+44)1223-336-033; or Email: deposit@ccdc.cam.ac.uk

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