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Two polymorphs of a lead(II) complex with 8-hydroxy-2-methylquinoline and thiocyanate

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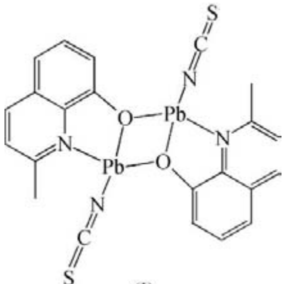
Two distinct polymorphs of bis(μ_2-methylquinolin-8-olato)-$\kappa^3N,O:O;\kappa^3O:N,O$-bis[(isothiocyanato-$\kappa N$)lead(II)], [$Pb_2(C_{10}H_8NO)_2(NCS)_2$], (I), forming dinuclear complexes from a methanolic solution containing lead(II) nitrate, 2-methylquinolin-8-ol (M-Hq) and KSCN, crystallized concomitantly as colourless prisms [form (I*a*)] and long thin colourless needles [form (I*b*)]. In both cases, the complexes lie across a centre of inversion. The polymorphs differ substantially in their conformation and in their interactions, *viz*. Pb$\cdots$S and π–π for form (I*a*) and Pb$\cdots$S, Pb$\cdots\pi$ and C—H$\cdots\pi$ for form (I*b*).

Comment

The synthesis of novel organic–inorganic hybrid materials in the field of supramolecular and crystal engineering has been a subject of rapid growth in recent years (Moulton & Zaworotko, 2001). Bidentate ligands containing soft and hard atoms have potential applications in catalytic and stoichiometric reactions (Kaim & Schwederski, 1995), as well as in advanced materials (Soldatov *et al.*, 2004). Recent reports of quinolin-8-ol (Hq) and its derivatives with lead(II) salts include [$Pb(q)(NCS)$]$_n$ (Shahverdizadeh *et al.*, 2008), [$Pb_2(M\text{-}q)_2(NO_3)_2(CH_3OH)_2$] (M-q is 2-methylquinolin-8-olate; Mohammadnezhad *et al.*, 2009*a*), [$Pb_2(M\text{-}q)_2(C_2H_3O_2)_2$] (Mohammadnezhad *et al.*, 2009*b*), [$Pb_2(Cl\text{-}q)_2(C_2H_3O_2)_2$] (Cl-q is 5-chloroquinolin-8-olate; Mohammadnezhad *et al.*, 2009*c*) and [$Pb_4(q)_6(NO_3)_2$] (Zhang *et al.*, 2008).

As part of our interest in exploring the effect of steric hindrance in lead(II) complexes with mixed ligands, we have examined isothiocyanate due to its various coordination modes, *i.e.* single or bridging coordination through S, N or both, in the presence of 2-methylquinolin-8-ol (M-Hq). In this paper, we report the crystal structures of two polymorphs of [$Pb(M\text{-}q)(NCS)$]$_2$, (I*a*) and (I*b*), which show that the steric hindrance of a methyl group leads to the coordination of isothiocyanate only *via* the N atom, not *via* the S atom, in contrast with the bidentate coordination observed in [$Pb(q)(NCS)$]$_n$ (Shahverdizadeh *et al.*, 2008).



(I)

Polymorph (I*a*) crystallizes in the triclinic space group $P\overline{1}$, while polymorph (I*b*) crystallizes concomitantly in the

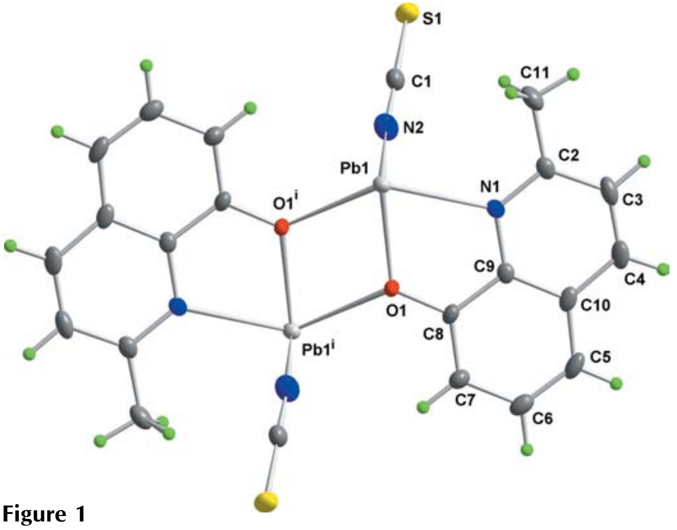


Figure 1
The structure of polymorph (I*a*), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) $-x, -y + 1, -z + 1$.]

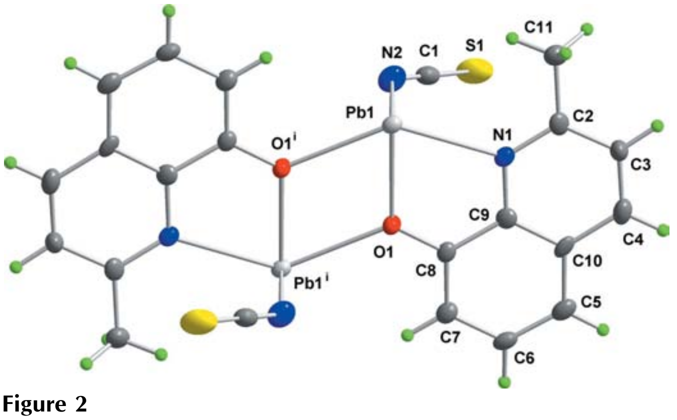


Figure 2
The structure of polymorph (I*b*), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) $-x + 1, -y + 2, -z + 1$.]

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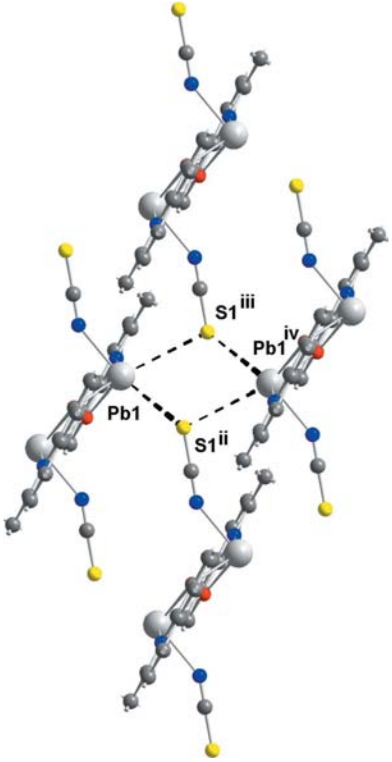

Figure 3
The Pb$\cdots$S interactions (dashed lines) in (I*a*). [Symmetry codes: (ii) $1 + x, y, z$; (iii) $-1 - x, 1 - y, 2 - z$; (iv) $-x, 1 - y, 2 - z$.]

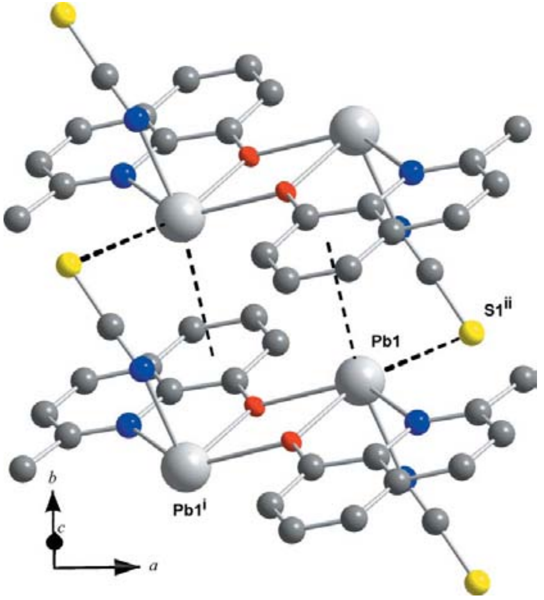

Figure 4
The Pb$\cdots$S interactions (dashed lines) in (I*b*), with distances of 3.506 (3) Å. The distance from atom Pb1 to the centroid of the C5–C10 ring of an adjacent molecule (also dashed lines) is 3.171 Å. [Symmetry codes: (i) $-x + 1, -y + 2, -z + 1$; (ii) $x, y + 1, z$.]

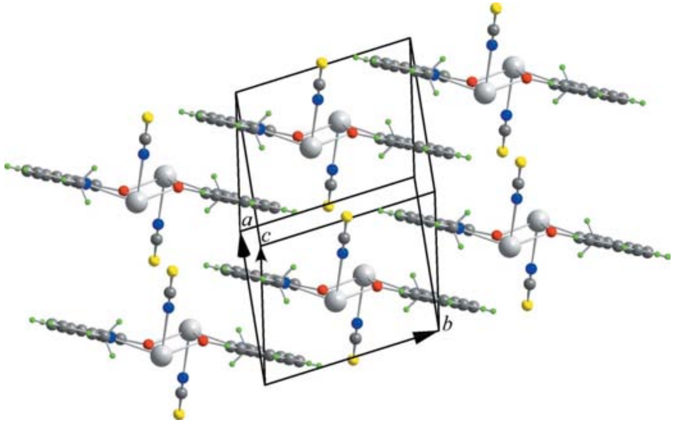

Figure 5
The contents of the unit cell of (I*a*), in a projection parallel to the quinoline rings.

monoclinic space group $P2_1/c$. Perspective drawings of these compounds are shown in Figs. 1 and 2, respectively; in both cases, the Pb_2O_2 core lies across the crystallographic inversion centre. In both structures, the Pb^{II} ion is four-coordinated, with the M-q ligand acting as a bidentate chelate, along with a bridging phenoxy O atom and the N atom from the isothiocyanate. As expected, these four coordinating atoms around the Pb^{II} centre in both polymorphs show a hemidirected geometry with a stereochemically active lone pair. Selected bond distances and bond angles are presented in Table 1. It is notable that the major structural difference between these two polymorphs is the NCS coordination angle. In (I*a*), the Pb1—N2—C1 angle is 149.7 (4)°, in contrast with a value of 136.8 (6)° in (I*b*). All other angles except O1—Pb1—N2, N2—Pb1—O1^{i} and O1^{i}—Pb1—N1 are similar [symmetry code: (i) $-x, -y + 1, -z + 1$ for (I*a*); (i) $-x + 1, -y + 2, -z + 1$ for (I*b*)]. The different conformations of the polymorphs are strongly reflected in the torsion angles containing thiocyanate atoms N2 and C1, but also in the torsion angle Pb1—O1—C8—C7 (see Table 1). The Pb$\cdots$Pb distances are 3.9397 (3) and 4.0212 (14) Å for (I*a*) and (I*b*), respectively.

Interestingly, in contrast with the previously reported coordination polymer $[Pb(q)(SCN)]_n$ (Shahverdizadeh *et al.*, 2008), the steric hindrance imposed by the methyl group at the C2 position prevents the coordination of SCN as a bidentate ligand. Indeed, the larger S atom is unable to coordinate to the Pb^{II} ion in either case, and hence the polymeric nature is disrupted and the coordination number decreases to four. Nevertheless, Pb$\cdots$S interactions are formed for Pb1$\cdots$S1^{ii} and Pb$^{iv}\cdots$S1^{iii} [3.6009 (14) Å] and for Pb1$\cdots$S1^{iii} and Pb$^{iv}\cdots$S1^{ii} [3.6649 (14) Å] in compound (I*a*) (Fig. 3) [symmetry codes: (ii) $1 + x, y, z$; (iii) $-1 - x, 1 - y, 2 - z$; (iv) $-x, 1 - y, 2 - z$]. Different types of interaction are seen in polymorph (I*b*). In addition to Pb$\cdots$S interactions with distances of 3.506 (3) Å, an interaction is observed between the Pb^{II} ion and the centroid (*Cg*) of the C5–C10 benzene ring in the molecule at the symmetry position ($x, y + 1, z$), with Pb$\cdots$*Cg* = 3.171 Å (Fig. 4).

Structure (I*a*) contains sheets of molecules in the *ac* plane held together by Pb$\cdots$S interactions (Fig. 5). The sheets have the aromatic wings of the ligand protruding from each side and interdigitate to provide π–π stacking, with perpendicular distances of 3.288 and 3.377 Å (Fig. 6), reflecting the different

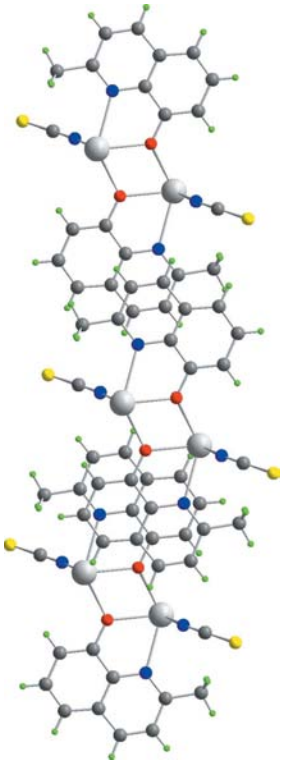

Figure 6
The π–π interactions in (I*a*). The overlap of the quinoline rings with a perpendicular distance of 3.288 Å is shown in the upper part, and that with a perpendicular distance of 3.377 Å is shown in the lower part.

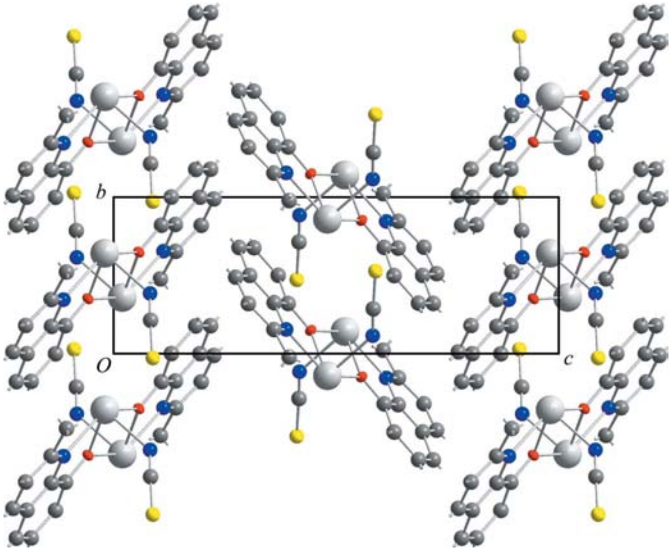

Figure 7
The herringbone formation of the aromatic surfaces in (I*b*). H atoms have been omitted for clarity.

positions of the N atoms in the overlapping heterocyclic rings.

In contrast, structure (I*b*) contains chains of molecules along *b* which are held together by Pb···S and Pb···ring interactions. The aromatic surfaces protruding from these chains make a herringbone formation in the *bc* plane (Fig. 7), with C—H···π interactions for enhancement [between C6—H6 and the centroid (*Cg*) of the C5–C10 ring at symmetry position ($-x + 1$, $y - \frac{1}{2}$, $-z + \frac{3}{2}$), with C6···*Cg* = 3.458 (7) Å, H6···*Cg* = 2.70 Å and C6—H6···*Cg* = 137°].

Experimental

Lead nitrate (0.33 g, 1 mmol), 2-methylquinolin-8-ol (0.16 g, 1 mmol) and KSCN (0.19 g, 2 mmol) were loaded into a convection tube. The tube was filled carefully with methanol and kept at 333 K. Crystals were collected from the side arm after several days; they were a mixture of large crystals of KNO_3, colourless prisms of (I*a*) and long thin colourless needles of (I*b*).

Polymorph (I*a*)

Crystal data

$[Pb_2(C_{10}H_8NO)_2(NCS)_2]$
$M_r = 846.89$
Triclinic, $P\overline{1}$
$a = 7.8556$ (5) Å
$b = 8.4155$ (5) Å
$c = 9.1550$ (6) Å
$\alpha = 78.524$ (1)°
$\beta = 69.771$ (1)°
$\gamma = 82.813$ (1)°
$V = 555.50$ (6) Å^3
$Z = 1$
Mo $K\alpha$ radiation
$\mu = 15.35$ mm^{-1}
$T = 173$ K
0.43 × 0.21 × 0.06 mm

Data collection

Siemens SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.095$, $T_{max} = 0.399$
9987 measured reflections
3889 independent reflections
3475 reflections with $I > 2\sigma(I)$
$R_{int} = 0.046$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.072$
$S = 1.00$
3889 reflections
146 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 2.27$ e Å^{-3}
$\Delta\rho_{min} = -3.09$ e Å^{-3}

Polymorph (I*b*)

Crystal data

$[Pb_2(C_{10}H_8NO)_2(NCS)_2]$
$M_r = 846.89$
Monoclinic, $P2_1/c$
$a = 12.037$ (5) Å
$b = 5.731$ (2) Å
$c = 16.327$ (6) Å
$\beta = 90.368$ (7)°
$V = 1126.3$ (7) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 15.14$ mm^{-1}
$T = 173$ K
0.96 × 0.04 × 0.02 mm

Data collection

Siemens SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.102$, $T_{max} = 0.752$
12903 measured reflections
3502 independent reflections
2528 reflections with $I > 2\sigma(I)$
$R_{int} = 0.078$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.090$
$S = 1.01$
3502 reflections
146 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 2.42$ e Å^{-3}
$\Delta\rho_{min} = -3.27$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I*a*) and (I*b*).

	(I*a*)	(I*b*)
Pb1—O1	2.272 (3)	2.295 (4)
Pb1—O^{i}	2.459 (3)	2.504 (4)
Pb1—N1	2.499 (4)	2.540 (5)
Pb1—N2	2.418 (4)	2.393 (6)
Pb1—O1—Pb1^{i}	112.70 (11)	113.76 (18)
O1—Pb1—O1^{i}	67.30 (11)	66.24 (18)
O1—Pb1—N1	69.09 (11)	68.97 (16)
O1—Pb1—N2	101.34 (15)	88.8 (2)
N1—Pb1—N2	80.77 (14)	80.6 (2)
N1—Pb1—O1^{i}	128.43 (11)	134.17 (16)
N2—Pb1—O1^{i}	82.10 (13)	89.17 (19)
Pb1—N2—C1	149.7 (4)	136.8 (6)
N1—Pb1—O1—C8	10.5 (3)	1.6 (4)
N1—Pb1—O1—Pb1^{i}	−151.77	−170.1 (2)
N2—Pb1—O1—C8	85.9 (3)	82.0 (5)
N2—Pb1—O1—Pb1^{i}	−76.35 (16)	−89.7 (2)
O1^{i}—Pb1—O1—C8	162.2 (4)	171.7 (5)
O1—Pb1—N1—C2	178.1 (4)	−178.8 (6)
O1—Pb1—N1—C9	−9.2 (3)	−2.9 (4)
N2—Pb1—N1—C2	72.1 (4)	88.9 (5)
N2—Pb1—N1—C9	−115.2 (3)	−95.2 (4)
O1^{i}—Pb1—N1—C2	144.3 (4)	168.5 (5)
O1^{i}—Pb1—N1—C9	−43.1 (4)	−15.6 (5)
O1—Pb1—N2—C1	−159.3 (7)	−68.8 (8)
N1—Pb1—N2—C1	−92.9 (7)	0.1 (8)
O1^{i}—Pb1—N2—C1	135.9 (8)	−135.0 (8)
O1—Pb1—O1^{i}—C8^{i}	161.3 (4)	171.3 (5)
N1—Pb1—O1^{i}—Pb1^{i}	34.3 (2)	13.0 (3)
N1—Pb1—O1^{i}—C8^{i}	−164.4 (3)	−175.7 (4)
N2—Pb1—O1^{i}—Pb1^{i}	105.85 (17)	89.0 (2)
N2—Pb1—O1^{i}—C8^{i}	−92.8 (4)	−99.7 (5)
Pb1—O1—C8—C7	169.5 (4)	−178.9 (5)
Pb1—O1—C8—C9	−10.9 (6)	−0.2 (8)
Pb1^{i}—O1—C8—C7	−30.5 (6)	−8.2 (8)
Pb1^{i}—O1—C8—C9	149.2 (3)	170.5 (4)
Pb1—N1—C2—C3	172.4 (3)	174.1 (5)
Pb1—N1—C2—C11	−8.6 (6)	−8.8 (9)
Pb1—N1—C9—C8	7.6 (5)	3.9 (7)
Pb1—N1—C9—C10	−171.8 (3)	−176.8 (5)

Symmetry codes: (i) $-x, -y+1, -z+1$ for (I*a*); (i) $-x+1, -y+2, -z+1$ for (I*b*).

Aromatic H atoms were included in the model with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C), and their positions were constrained to ideal geometry using an appropriate riding model, with C—H = 0.95 Å. For methyl groups, N—C—H angles (109.5°) were kept fixed, while the torsion angle was allowed to refine, with the starting positions based on the circular Fourier synthesis averaged using the local threefold axis; C—H = 0.98 Å and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C).

For both polymorphs, data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT* and *SADABS* (Sheldrick, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2009); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3124). Services for accessing these data are described at the back of the journal.

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