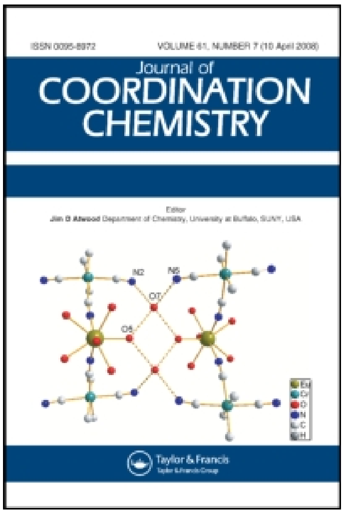

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A new lead(II) complex of 2,2'-bipyridine, acetate and thiocyanate ligands: synthesis, characterization and crystal structure of [Pb(bpy)(NCS)(CH$_3$COO)]_n

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A NEW LEAD(II) COMPLEX OF 2,2′-BIPYRIDINE, ACETATE AND THIOCYANATE LIGANDS: SYNTHESIS, CHARACTERIZATION AND CRYSTAL STRUCTURE OF [Pb(bpy)(NCS)(CH$_3$COO)]$_n$

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A new lead(II) complex of 2,2′-bipyridine (bpy), acetate and thiocyanate has been synthesized and characterized by C H N elemental analysis, IR, ^{1}H NMR, ^{13}C NMR and ^{207}Pb NMR spectroscopy. The structure of [Pb(bpy)(NCS)(CH$_3$COO)]$_n$ was confirmed by X-ray crystallography. Single-crystal X-ray data show the complex to be a one-dimensional polymer as a result of thiocyanate ligand bridging with the basic repeating monomeric units [Pb(bpy)(NCS)(CH$_3$COO)]. The Pb atom has an unsymmetrical five-coordinate geometry, being coordinated by two nitrogen atoms of bpy, two oxygen atoms of the acetate and one nitrogen atom of the thiocyanate anion. The arrangement of the bpy, acetate and nitrate ligands exhibits a coordination gap around the Pb(II) ion, occupied possibly by a stereoactive lone pair of electrons on lead(II), and the coordination around the lead atoms is hemidirected. There are π–π stacking interactions between the parallel aromatic rings.

Keywords: Lead(II) complex; Crystal structure; Mixed-anion complexes; 2,2′-Bipyridine ligand

INTRODUCTION

Recent reports of the crystal structure of 1 : 1 adducts of [Pb(phen)(O$_2$CCH$_3$)(O$_2$ClO$_2$)] [1], [Pb(phen)(O$_2$CCH$_3$)(O$_2$NO)] [2] and [Pb(phen)(O$_2$CCH$_3$)(NCS)] [3] and the 1 : 2 adduct of [Pb(phen)$_2$(CH$_3$COO)]X (phen = 1,10-phenanthroline; X = NCS$^-$, NO$_3^-$ and ClO$_4^-$) [4] show the presence of bridging acetate and its influence on the coordination stereochemistry of the lead(II) ion and also on their structures. In the present paper, we report the synthesis and characterization of a new 1 : 1 adduct of [Pb(bpy)(NCS)(CH$_3$COO)]$_n$ (bpy = 2,2′-bipyridine). The importance of the mixed-anion lead(II) complexes is due to the influence of different ligands on the structure

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and lone pair activity of the lead(II) complexes, with the main coordination sphere being unchanged.

EXPERIMENTAL

Physical Measurements

IR spectra were recorded as nujol mulls using Perkin-Elmer 597 and Nicolet 510P spectrophotometers. Microanalyses were carried out using a Heraeus CHN-O-Rapid analyzer. Melting points were measured on an Electrothermal 9100 instrument and were uncorrected. ^{207}Pb solution NMR spectra were recorded on a Bruker DRX-500 Avance spectrometer at 104.6 MHz using a 5-mm broadband probe. Lead chemical shifts are reported (ppm) downfield from tetramethyllead using $PbPh_4$ ($\delta_{Pb} = -178.0$ ppm, saturated in $CDCl_3$) as an external standard in 0.01 M at 25°C. Each lead spectrum was acquired in 3–10 h.

Preparation of [Pb(bpy)(NCS)(CH_3COO)]

2,2′-Bipyridine (0.156 g, 1 mmol) was placed in one arm of a branched tube and a mixture of lead(II) acetate (0.36 g, 1 mmol) and potassium thiocyanate (0.097 g, 1 mmol) in the other. Methanol was carefully added to fill both arms, then the tube was sealed and the ligand-containing arm immersed in an oil bath at 60°C, while the other arm was kept at ambient temperature. After seven days, white crystals (mp 225°C) had deposited in the cooler arm. Yield: 0.216 g, 45%. Anal. Calcd. for $C_{13}H_{11}N_3O_2PbS$(%): C, 32.43; H, 2.28; N, 8.73. Found: C, 32.30; H, 2.30; N, 8.70. IR (cm^{-1}) selected bonds: 850(s), 1420(s), 1580(s), 1650(s), 2020(vs), 2980(w), 3140(w). ^{1}H NMR (DMSO; δ): 1.70 (s, 3H), 7.80 (t, 2H), 8.30 (q, 2H), 8.70 (d, 2H), 7.80 (d, 2H) ppm. ^{13}C{^{1}H} NMR (DMSO; δ): 27.50 ($^{13}CH_3$–COO), 178.70 (CH_3–^{13}COO), 117.50, 124.20, 127.60, 1141.60, 149.95, 150.65 ppm. ^{207}Pb NMR (DMSO; δ): −1450 ppm.

X-ray Crystallography

Crystallographic measurements were made at 173(2) K using a Siemens R3m/V diffractometer. The intensity data were collected within the range $1.97 \leq \theta \leq 28.25°$ using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Accurate unit cell parameters and an orientation matrix for data collection were obtained from least-squares refinement. Intensities of 15 849 unique reflections were measured, from which 3328 with $I > 2\sigma(I)$ were used in the refinement. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2.

The positions of hydrogen atoms were idealized and included in the calculations of the structure factors as fixed contributions. Each hydrogen atom was assigned an isotopic thermal parameter R; R_w with goodness-of-fit on $F^2 = 1.015$, $R = 0.0265$, $R_w = 0.06721$. The final difference density map showed a maximum peak and hole of 1.900 and −1.310 e Å^{-3}, respectively. Corrections for Lorentz and polarization effects, as well as the empirical correction for absorption using the Sadabs program, were applied. All structural calculations were carried out with a PDP-11/23+ computer using the SDP-PLUS program package [5,6].

TABLE I Crystal data and structure refinement details for [Pb(bpy)(NCS)(CH_3COO)]

Empirical formula	$C_{13}H_{11}N_3O_2PbS$
Formula weight	480.50
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2(1)/c$
Unit cell dimensions	$a = 6.5429(5)$ Å, $\alpha = 90.00°$
	$b = 13.5746(9)$ Å, $\beta = 97.5610(10)°$
	$c = 16.1719(11)$ Å, $\gamma = 90.00°$
Volume	1423.85(17) $Å^3$
Z	4
Density (calculated)	2.241 $Mg\,m^{-3}$
Absorption coefficient	11.999 mm^{-1}
$F(000)$	896
Crystal size	$0.35 \times 0.26 \times 0.12$ mm
Theta range for data collection	1.97 to 28.25
Index ranges	$-8 \leq h \leq 8$, $-17 \leq k \leq 18$, $-17 \leq l \leq 21$
Reflections collected	15 849
Independent reflections	3328 [R(int) = 0.0363]
Completeness to theta = 28.25	94.4%
Absorption correction	Semiempirical from equivalents
Max. and min. transmission	0.3270 and 0.1020
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3328/0/181
Goodness-of-fit on F^2	1.056
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0265$, $wR2 = 0.0672$
R indices (all data)	$R1 = 0.0305$, $wR2 = 0.0690$
Largest diff. peak, hole	−1.310, 1.900 e $Å^{-3}$

Crystal data and structure refinement are given in Table I. Atomic coordinates and equivalent isotropic displacement parameters are given in Table II. Selected bond lengths and angles are given in Table III. Anisotropy thermal parameters, observed and calculated structure factors, full lists of bond distances, bond angles and torsion angles are given in the supplementary material. ORTEP diagrams and a perspective view of the packing in the unit cells are shown in Figs. 1 and 2.

DISCUSSION

Synthesis

Reaction between 2,2′-bipyridine and an equimolar mixture of lead(II) acetate and potassium thiocyanate by diffusion along a thermal gradient in methanol solution (the branched tube method) provided crystalline material analyzing as [Pb(bpy)(NCS)(CH_3COO)].

The IR spectrum of [Pb(bpy)(NCS)(CH_3COO)] shows ν(COO) at *ca* 1420 and 1580 cm^{-1}, and also ν(SCN) at *ca* 2020 cm^{-1}, very similar to other lead(II) complexes, such as [Pb(phen)$_2$(NO_3)(NCS)] (2020 cm^{-1}) [7], [Pb(phen)(O_2CCH_3)(NCS)] (2040 cm^{-1}) [3] and [Pb(phen)$_2$(O_2CCH_3)(NCS)] (2040 cm^{-1}) [4], but significantly different than mercury(II) complexes, for example [Hg(bq)$(SCN)_2$] (bq = 2,2′-biquinoline) (2070 cm^{-1}) [8] and [Hg(DABTZ)$(SCN)_2$] (DABTZ = 2,2′-diamino-4,4′-bithiazole)

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for Pb(bpy)(CH_3COO)(NCS). *U*(eq) is defined as one-third of the trace of the orthogonalized *Uij* tensor

	x	*y*	*z*	*U*(eq)
Pb(1)	942(1)	3342(1)	87(1)	27(1)
C(1)	4286(6)	1859(3)	−631(3)	27(1)
C(2)	5216(6)	1233(3)	−1140(3)	31(1)
C(3)	4251(6)	1050(3)	−1936(3)	32(1)
C(4)	2355(6)	1488(3)	−2195(3)	28(1)
C(5)	1483(5)	2104(3)	−1652(2)	20(1)
C(6)	−551(5)	2589(2)	−1893(2)	20(1)
C(7)	−1690(6)	2467(3)	−2667(2)	27(1)
C(8)	−3571(6)	2941(3)	−2847(3)	32(1)
C(9)	−4284(6)	3517(3)	−2246(3)	31(1)
C(10)	−3072(6)	3604(3)	−1481(3)	28(1)
C(11)	6281(6)	4294(3)	853(2)	27(1)
C(12)	347(6)	1459(3)	794(3)	27(1)
C(13)	−48(7)	474(3)	1172(3)	40(1)
N(1)	2460(4)	2290(2)	−879(2)	21(1)
N(2)	−1239(5)	3153(2)	−1305(2)	23(1)
N(3)	4937(6)	3800(3)	560(3)	48(1)
O(1)	2010(4)	1905(2)	1024(2)	37(1)
O(2)	−1001(4)	1818(2)	253(2)	36(1)
S(1)	8179(2)	4989(1)	1281(1)	34(1)

TABLE III Selected bond lengths (Å) and angles (°) for Pb(bpy)(CH_3COO)(NCS)

Pb(1)–N(1)	2.424(3)	Pb(1)–N(3)	2.698(4)
Pb(1)–O(2)	2.461(3)	Pb(1)–C(12)	2.847(4)
Pb(1)–O(1)	2.513(3)	Pb(1)–S(1)	3.593(4)
Pb(1)–N(2)	2.516(3)	Pb–Pb	4.665(4)
S(1)–N(3)	3.218(4)		
N(1)–Pb(1)–O(2)	80.56(11)	O(1)–Pb(1)–N(3)	79.97(11)
N(1)–Pb(1)–O(1)	79.96(11)	N(2)–Pb(1)–N(3)	133.75(12)
O(2)–Pb(1)–O(1)	52.29(9)	N(1)–Pb(1)–C(12)	79.56(11)
N(1)–Pb(1)–N(2)	66.11(10)	O(2)–Pb(1)–C(12)	26.10(11)
O(2)–Pb(1)–N(2)	76.76(10)	O(1)–Pb(1)–C(12)	26.19(10)
O(1)–Pb(1)–N(2)	122.70(10)	N(2)–Pb(1)–C(12)	100.14(11)
N(1)–Pb(1)–N(3)	81.63(12)	N(3)–Pb(1)–C(12)	105.76(12)
O(2)–Pb(1)–N(3)	131.15(11)		

($2065\,cm^{-1}$) [9]. This suggests different coordination via nitrogen of the thiocyanate anions in this complex compared with the mercury(II) complexes.

Attempts to isolate [Pb(bpy)$_2$(NCS)(CH_3COO)] were unsuccessful and each time the 1 : 1 adduct was isolated.

Crystal Structure of [Pb(bpy)(NCS)(CH_3COO)]$_n$

The crystal structure of this compound consists of polymeric units of [Pb(bpy)(NCS)(CH_3COO)]$_n$. Each lead atom is chelated by two nitrogen atoms of the bpy ligand with Pb–N distances of 2.516(3) and 2.424(3) Å and the acetate anions with Pb–O distances of 2.461(3), and 2.513(3) Å. The nitrogen of the thiocyanate anion completes the coordination with a Pb–N distance of 2.698(4) Å (Table II).

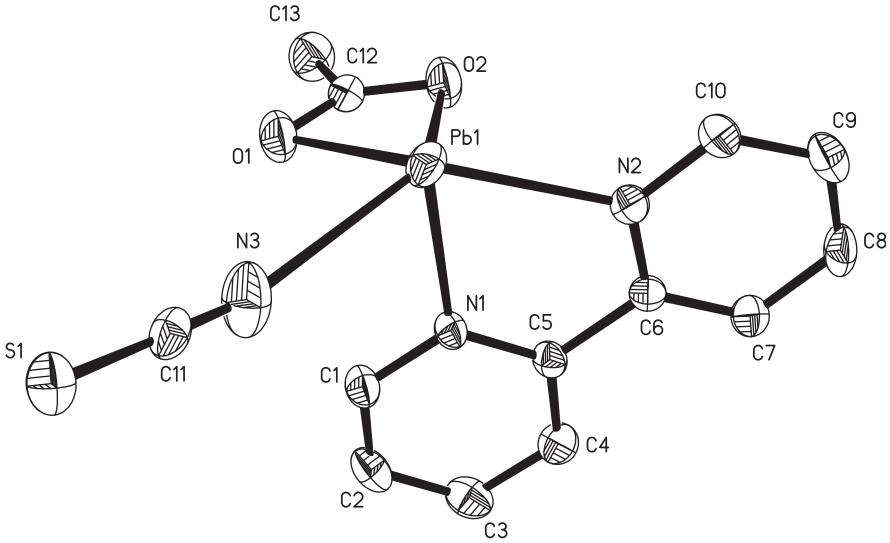


FIGURE 1 ORTEP diagram of [Pb(bpy)(CH_3COO)(NCS)].

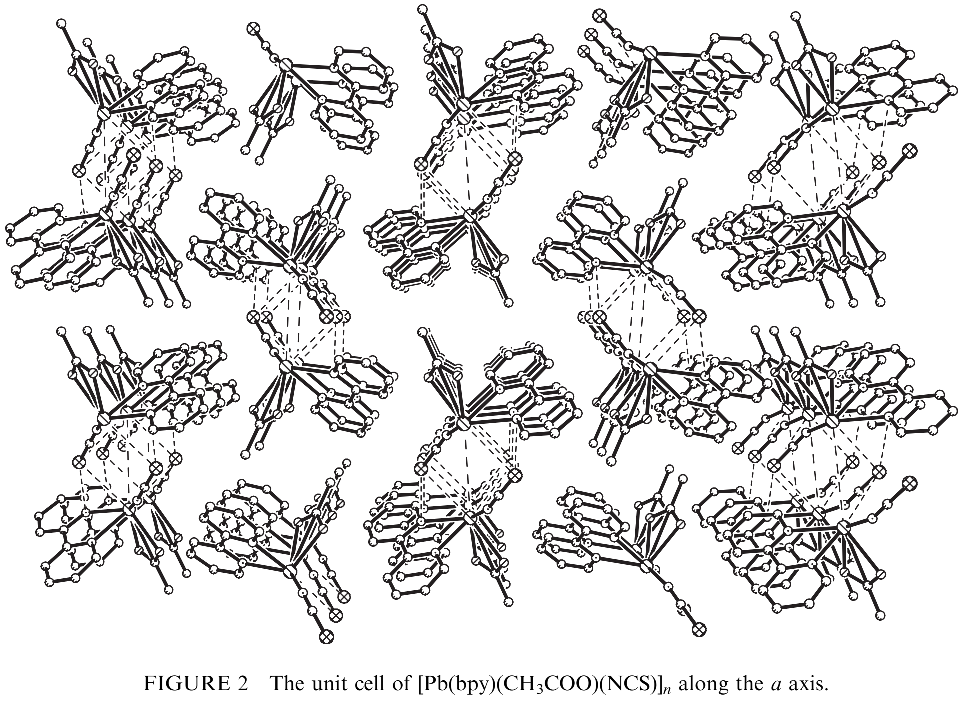


FIGURE 2 The unit cell of $[Pb(bpy)(CH_3COO)(NCS)]_n$ along the *a* axis.

The coordination number in this complex is five (two ‘bpy’ ligands, two acetate anions and one thiocyanate anion); interaction of lead(II) with sulfur atoms of adjacent thiocyanate produces the polymeric units. In fact each atom Pb in this structure, along with five normal bonds, forms one “weak” Pb···S bond and the exact distance is 3.593(4) Å (Table II). The Pb···Pb distance in the polymeric units is 4.665(4) Å.

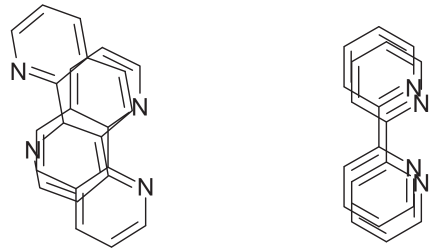
There is a weak interaction between one sulfur atom (S1) of thiocyanate ligand with a nitrogen atom (N3) of bpy ligand from adjacent molecules (Fig. 2), N(3)···S(1) = 3.218(4) Å (Table II).

The arrangement of bpy, acetate and thiocyanate suggests a gap or hole in the coordination geometry around the metal ion [O(2)–Pb–N(3) angle is 131.15(11)°], occupied possibly by a stereoactive lone pair of electrons on lead(II). The observed shortening of the Pb–O bonds on the side of the Pb(II) ion opposite the putative lone pair [2.461(4) Å compared with 2.513(4) Å adjacent to the lone pair] supports this arrangement [10]. Hence, the geometry of the nearest coordination environment of every lead atom is likely to be caused by the geometrical constraints of the coordinated bpy ligand, acetate and thiocyanate anions and by the influence of a stereochemically active lone pair of electrons in a hybrid orbital on the metal atom. Such an environment leaves space for bonding of the sulfur atoms of the thiocyanate of adjacent molecules (Fig. 2). The presence of a lone pair on lead seems to be the reason that the bridging interactions are not shorter. If the stereochemically active lone pair was not present, it might create more bridging interaction between lead(II) and neighboring oxygen and thiocyanate. Consequently, this phenomenon could lead to more symmetry.

Despite some similarities in $Pb(L)(CH_3COO)(NCS)$ (L = bpy and phen), there are significant differences between the complex reported here and $[Pb(phen)(CH_3COO)(NCS)]_2$ [3], showing the influence of different ligands on the structure of the complexes. In the $[(phen)Pb(O_2CCH_3)(NCS)]$ complex, acetate oxygen atoms are bridged, forming dimeric units, and the thiocyanate is monodentate towards the lead atom but does not seem to be involved in further bridging interactions. In $[Pb(bpy)(NCS)(CH_3COO)]_n$, the acetate oxygen atoms are not bridged and interactions of lead(II) with sulfur atoms of the thiocyanate produce polymeric units in the solid state. Indeed, the above-mentioned compound is a rarely observed 1D framework and a new mixed-ligand complex containing three ligands simultaneously coordinated in its crystal structure.

The possible stereochemical activity of the lone pair in divalent lead compounds has been discussed by Shimoni-Livny *et al.* based on a thorough review of crystal data available in the Cambridge Structural Database (CSD) [11]. They classify lead coordination as holodirected, which refers to complexes in which the bonds to ligand atoms are directed throughout the surface of an encompassing sphere, while hemidirected refers to those cases in which the bonds to ligand atoms are directed through only part of the coordination sphere, leaving a gap in the distribution of bonds to the ligand. The latter, present in all Pb(II) compounds with coordination number 2 to 5, is fairly common in Pb(II) compounds with coordination numbers 6, 7 and 8, and does not exist in lead complexes with higher coordination numbers, where holodirected geometry is the rule. For the structure described here, coordination around the lead atoms is hemidirected with a significant gap *trans* to the chelating acetate ligand.

A striking similarity between $[Pb(phen)(NCS)(CH_3COO)]_2$ and $[Pb(bpy)(NCS)(CH_3COO)]_n$ is found in the π–π stacking [12,13] interaction between the parallel aromatic rings of adjacent chains, as shown in Fig. 3. The mean molecular planes are close to parallel and separated by a distance of *ca* 3.5 Å, close to that of the planes in graphite. Parallel arrays of planes of aromatic moieties indicate that these interactions are of the "pi-stacking" type, rather than "edge-to-face" or "vertex-to-face" types [14–17]. Projection of the structure perpendicular to the ring plane shows the overall form of the "slipped" stacking [17,18], which is at least



$[Pb(phen)(NCS)(CH_3COO)]_n$ $[Pb(bpy)(NCS)(CH_3COO)]_n$

FIGURE 3 Projection of nearest neighbor pairs in the π–π stacks of heteroaromatic bases in $[Pb(L)(NCS)(CH_3COO)]_n$ (L = phen and bpy).

qualitatively understandable in terms of optimizing approaches between atoms of opposite charges [19].

A simple model to describe the nature of π–π interactions has been developed by Hunter *et al.* [19]. This model predicts that face-to-face π-stacked interactions will be disfavored due to π–π repulsion. However, in offset π-stacked and edge-on or T-shaped geometries, favorable π–σ attractions dominate. The polarization of aromatic systems, through the introduction of heteroatoms, electron-withdrawing groups or electron-donating groups, alters the nature of the π–π interactions. For example, although it is well known that neither benzene [20] nor hexafluorobenzene tends to form stacked arrangements, the adduct between these two molecules adopts a structure comprising inclined stacks of alternating molecules [21]. Here, the hexafluorobenzene π-system is electron deficient with respect to benzene and this reduces the π–π repulsion, making the formation of offset π-stacked molecules more favorable. The introduction of heteroatoms can lead to a similar perturbation of aromatic interactions [22]; specifically, nitrogen atoms have been shown to remove electron density from the π-system, and hence have a similar effect to electron-withdrawing groups. It is known that electron-poor aromatic groups interact most strongly with electron-rich aromatic groups. Hence, it can be expected that within the $[Pb(phen)(NCS)(CH_3COO)]_2$ complex, interaction of the electron-poor pyridyl rings with less electron-poor rings such as phenyl groups in chains must be favored. As $[Pb(bpy)(NCS)(CH_3COO)]_n$ includes equally or almost equally electron-deficient, or indeed electron-rich, rings, it can be expected that within the molecule discussed here, model face-to-face π-stacked interactions must be disfavored due to the dominance of π–π repulsion.

Thus two factors, lone pair activity and π–π stacking, may control the coordination sphere of this complex. The obvious question then is whether the lone pair activity has stretched coordinate bonds resulting in ligand stacking or whether the stacking interaction has imposed a positioning of the donor atoms, forming a gap in the coordination sphere. As the model face-to-face π-stacked interactions must be disfavored due to π–π repulsion, lone pair activity may be the most important factor and affect π–π stacking.

Mercury(II) complexes coordinate the thiocyanate via the S atom; for example, $[Hg(DPBTZ)(SCN)_2]$ (DPBTZ = 2,2′-diphenyl-4,4′-bithiazole) [23], $[Hg(DABTZ)(SCN)_2]$ [9], $[Hg(L)(SCN)_2]$ (L = *N*-(2-pyridyl)carbonylaniline) [24] and $[Hg(bq)(SCN)_2]$ [8]. In the present lead complex and other lead(II) complexes,

$[Pb(phen)_2(NO_3)(NCS)]$ [7] and $[Pb(phen)(O_2CCH_3)(NCS)]$ [3], the thiocyanate is coordinated via the N atom, indicating that Pb^{2+} is harder than Hg^{2+}. Indeed lead is a borderline metal with high affinity for nitrogen donors and appears to bind to the harder base nitrogen.

The packing arrangement of the molecule discussed here is not only affected by a subtle interplay of competing weak forces, most notably π–π interactions and lone pair activity, but also Pb···C interactions are important. The Pb atom is linked with carbon atoms through intramolecular interactions with Pb···C separation of Pb(1)–C(12) = 2.847 Å. It appears that Pb in this complex has a monohapto intramolecular (η^1) interaction with the carbon of the acetate anion. Thus, rather than a PbN_3O_2 coordination sphere, the lead atom in this complex can be considered to coordinate with carbon on the side of Pb(II) adjacent to the Pb–N and Pb–O bonds and opposite the lone pair. Thus the lone pair may be involved in additional interaction with π^* orbitals of the acetate anion. This point shows the capacity of Pb(II) to act as both a Lewis acid and a Lewis base [25].

Acknowledgment

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Supplementary Material

Complete bond lengths and angles, coordinates and displacement parameters have been deposited at the Cambridge Crystallography Data Centre. Supplementary data are available on request from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk), quoting the deposition number 230242.

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