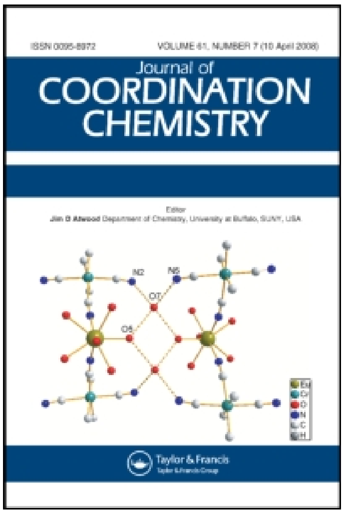

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Syntheses and Characterization of a New One-Dimensional Polymer Containing (μ-Thiocyanate)(bpy)Lead(II) Molecule and New Mixed-Anion Lead (II) Complexes: Crystal Structures of $[Pb(bpy)(SCN)_2]$*_n* (byp = 2,2'-Bipyridine) and $[Pb(phen)_2(NO_3)_{0.7}(ClO_4)_{0.3}](ClO_4)$ (phen = 1,10-Phenanthroline)

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SYNTHESES AND CHARACTERIZATION OF A NEW ONE-DIMENSIONAL POLYMER CONTAINING (μ-THIOCYANATE)(bpy)LEAD(II) MOLECULE AND NEW MIXED-ANION LEAD (II) COMPLEXES: CRYSTAL STRUCTURES OF $[Pb(bpy)(SCN)_2]_n$ (byp = 2,2′-BIPYRIDINE) AND $[Pb(phen)_2(NO_3)_{0.7}(ClO_4)_{0.3}](ClO_4)$ (phen = 1,10-PHENANTHROLINE)

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Complexes $[Pb(bpy)(SCN)_2]_n$ (bpy = 2,2′-bipyridine), [Pb $(phen)_2(NO_3)_{0.7}(ClO_4)_{0.3}](ClO_4)$, $Pb(phen)_2(SCN)(NO_3)$, and $Pb(phen)_2(SCN)(ClO_4)$ (phen = 1,10-phenanthroline)], have been synthesized using a direct reaction between $Pb(NO_3)_2$ and ligands. The complexes have been isolated and characterized by IR-spectra and CHN-elemental analysis. The structures of $[Pb(bpy)(SCN)_2]_n$ and $[Pb(phen)_2(NO_3)_{0.7}(ClO_4)_{0.3}](ClO_4)$ have been confirmed by X-ray crystallography. The single crystal X-ray crystallography of a new one-dimensional complex of Pb(II) with 2,2′-bipyridine, $[Pb(bpy)(SCN)_2]_n$, shows the complex to be polymeric as a result of thiocyanate ligand bridging. The Pb atom being in a unsymmetrical eight-coordinate, N_4S_4, environment and the arrangement of the 2,2′-bipyridine, thiocyanate anion suggest a gap in coordination geometry around the Pb(II) ion, occupied possibly by a stereoactive lone pair of electrons on lead (II) and the coordination around atoms is hemi-directed. There is a π–π interaction between the aromatic rings of the interchains in $[Pb(bpy)(SCN)_2]_n$, this stacking causes the complex to be more stable. An attempt to isolate single crystals of $Pb(phen)_2(NO_3)(ClO_4)$ from water led to the isolation of $[Pb(phen)_2(NO_3)_{0.7}(ClO_4)_{0.3}](ClO_4)$. The single crystal X-ray study shows the complex to be monomeric. The Pb atom lies in an unsymmetrical six-coordinate, N_4O_2, environment and the arrangement of the 1,10-phenanthrolines, suggest a gap in coordination geometry around the Pb(II) ion, occupied possibly by a stereoactive lone pair of electrons on lead (II) and the coordination around atoms is hemi-directed.

INTRODUCTION

The coordination chemistry of lead (II) with 1,10-phenanthroline and other *N*-donor ligands has been investigated in the past decade in considering the coordination and stereoactivity of valence shell lone-pair electrons [1–10]. Mixed-anion complexes [11–14], provide further examples. Extensive recent structural studies of lead (II)

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compounds in particular have provided a basis for detailed analysis of the evidence for coordination sphere distortions which may be a consequence of the presence of such pairs. It appears that in complexes of lead (II) (and probably in those of related species such as Tl(I)[15–21] and Bi(III) [22–29]), the nature and form of the coordination sphere is generally determined by a number of factors, possibly lone pair–bond pair repulsions, of comparable influence, so that seemingly minor differences in ligands or in the crystal array can have quite marked effects upon the coordination stereochemistry. Since the presence of lone pair is not directly detected but inferred on the basis of the spatial distribution of atoms assumed to be donors to the central metal, the identification of those donor atoms is fundamental to the analysis of any particular system. Interestingly, this alone is not a straightforward process. An interesting point is that crystal packing may affect the size and extent of the lone pair in the coordination sphere. In recent reports of the crystal structures of Pb(phen)(CH_3COO)(ClO_4) [11], Pb(phen)(CH_3COO)(NO_3) [12] and Pb(phen)(CH_3COO)(SCN) [14] we described the presence of the lone pair and its influence upon the coordination stereochemistry of lead (II). In this article, in order to provide further information about mixed-anion complexes, we isolated some of complexes, and determined the structure of [Pb(phen)$_2$(NO_3)$_{0.7}$(ClO_4)$_{0.3}$](ClO_4) and Pb(bpy)(SCN)$_2$; our results support the presence of a stereoactive valence shell electron lone pair on the lead atom.

EXPERIMENTAL

IR spectra were recorded for 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 apparatus and are uncorrected.

Preparation of the [Pb(bpy)(SCN)$_2$] Complex (I)

The title compound was synthesized by mixing a solution of 2,2′-bipyridine (0.088 g, 0.5 mmol) in hot ethanol (10 mL) and a hot aqueous solution of lead (II) nitrate (0.16 g, 0.5 mmol) and KSCN (0.049 g, 0.5 mmol). The resulting colorless solution was heated, stirred and left to evaporate at room temperature. After a few days, colorless crystals were isolated. Yield: 0.239 g, 50% m.p. 280°C (Found: C, 30.63; H, 1.80; N, 11.50. $C_{12}H_8N_4PbS_2$ requires: C, 30.03; H, 1.67; N, 11.69). IR (cm^{-1}) major bands only: 740(s), 1010(vs), 1110(vs), 1530(s), 1610(s), 2040(vs), 3050(w).

Branched Tube Method

2,2′-bipyridine (0.088 g, 0.5 mmol) was placed in one arm of the branched tube and a mixture of lead (II) nitrate (0.16 g, 0.5 mmol) and KSCN (0.049 g, 0.5 mmol) in the other. Methanol was carefully added to fill both arms, then the tube was sealed and the ligand-containing arm immersed in a bath at 60°C while the other was at ambient temperature. After 15 d, colorless crystals, m.p. 280°C had deposited in the cooler arm.

Preparation of [Pb(phen)$_2$(NO$_3$)$_{0.7}$(ClO$_4$)$_{0.3}$](ClO$_4$) (II)

Lead (II) nitrate (0.331 g, 1 mmol) was dissolved in water by heating and was added dropwise with stirring to an aqueous solution of 1,10-phenanthroline (0.4 g, 2 mmol) and NaClO$_4$ (0.245 g, 2 mmol). On standing, the product precipitated and was removed by filtration, washed with a little ice-cold water and recrystallized from a concentrated aqueous solution. The pure product was washed with ice-cold ethanol then diethyl ether before drying in air. Yield: 0.444 g, 60% m.p. 250° C (Found: C, 39.63; H, 2.08; N, 9.50. $C_{24}H_{16}ClN_5O_7Pb$ requires: C, 39.47; H, 2.19; N, 9.59). IR (cm^{-1}) major bands only: 720(s), 740(s), 1010(vs), 1110(vs), 1370(vs), 1530)s), 1610(s), 3050(w).

Preparation of Pb(phen)$_2$(SCN)(NO$_3$) (III) and Pb(phen)$_2$(SCN)(ClO$_4$) (IV)

We prepared Complexes III and IV via the analogous method used for the synthesis of the [Pb(phen)$_2$(NO$_3$)$_{0.7}$(ClO$_4$)$_{0.3}$](ClO$_4$) complex.

Complex III

Melting point 220°C.Yield: 0.480 g, 70%. (Found: C, 43.5; H, 2.32; N, 12.21. $C_{25}H_{16}N_6SO_3Pb$ requires: C, 43.6; H, 2.23; N, 12.3%). IR (cm^{-1}) selected bands: 720(s), 850(s), 1380(vs), 1590(s), 1648(s), 2040(vs), 3140(w).

Complex IV

Melting point 280°C. Yield: 0.362 g, 50% (Found: C, 41.25; H, 2.1; N, 9.7. $C_{25}H_{16}ClN_5SO_4Pb$ requires: C, 41.35; H, 2.2; N, 9.65%). IR (cm^{-1}) selected bands: 742(s), 1100(vs), 1580(s), 1660(s), 2045(vs), 3050(w).

Crystallography

Crystal Data and Refinement Details

[Pb(phen)$_2$(NO$_3$)$_{0.7}$(ClO$_4$)$_{0.3}$](ClO$_4$) · $C_{24}H_{16}Cl_{1.3}N_{4.7}O_{7.3}Pb$, M 740.29, triclinic, space group *P*-1, $a = 7.6641(17)$, $b = 12.126(3)$, $c = 13.051(3)$ Å, $\alpha = 95.068(4)$, $\beta = 102.203(4)$, $\gamma = 94.498(4)°$, $V = 1147.9(4)$ Å^3, D_c (Z = 2 f.u.) 2.093 mg/m^3, *F*(000) 711. Specimen: 0.30 mm × 0.3 mm × 0.3 mm; $T_{\max,\min} = 0.86$, 0.51, N 14393, N_0 6603, $R = 0.0275$, $R_w = 0.0661$.

[Pb(bpy)(SCN)$_2$] · $C_{12}H_8N_4PbS_2$, M 479.53, monoclinic, space group *C*2/*c*, $a = 17.653(10)$, $b = 12.029(7)$, $c = 6.793(4)$ Å, $\alpha = 90$, $\beta = 106.95(4)$, $\gamma = 90$, V = 1380.0 (14) Å^3, D_c ($Z = 4$ f.u.) 2.308 mg/m^3, *F*(000) 888. Specimen: 0.50 mm × 0.20 mm × 0.20 mm; $T_{\max,\min} =$ 0.1886, 0.0621, N 2043, N_0 1700, $R =$ 0.0247, $R_w =$ 0.587.

Determination of the Structures

Crystallographic measurements were made at 293(2) K for [Pb(bpy)(SCN)$_2$] and 110 K for [Pb(phen)$_2$(NO$_3$)$_{0.7}$(ClO$_4$)$_{0.3}$](ClO$_4$) using a Siemens R3m/V diffractmeter. The intensity data were collected within the range. $4 \le \theta \le 30.06°$ for [Pb(bpy)(SCN)$_2$] and $2.21 \le \theta \le 31.07°$ for [Pb(phen)$_2$(NO$_3$)$_{0.7}$(ClO$_4$)$_{0.3}$](ClO$_4$) using graphite monochromated Mo-*Kα* radiation (λ = 0.71073 Å). Accurate unit cell parameters and an orientation matrix for data collection were obtained from least-squares refinement. Intensities of 2043 and 14393 unique reflections were measured, from which 1986 and 7125 with $I > 2\sigma(I)$ were used in the refinement for [Pb(bpy)$(SCN)_2$] and [Pb$(phen)_2(NO_3)_{0.7}(ClO_4)_{0.3}$]($ClO_4$), respectively. The structures have been 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

TABLE I Crystal data and structure refinement for two complexes

Empirical formula	Pb(bpy)$(SCN)_2$ $C_{12}H_8N_4PbS_2$	[$Pb_1(Phen)_2$]$(ClO_4)_{1.3}(NO_3)_{0.7}$ $C_{24}H_{16}C_{11.3}N_{4.7}O_{7.3}Pb_1$
Formula weight	479.53	740.29
Temperature	293(2) K	110(2) K
Wavelength	0.71073 Å	0.71073
Crystal system	Monoclinic	Triclinic
Space group	*C*2/*c*	*P*-1
Unit cell dimensions	$a = 17.653(10)$ Å $\alpha = 90°$ $b = 12.029(7)$ Å $\beta = 106.95(4)°$ $c = 6.793(4)$ Å $\gamma = 90°$	$a = 7.6641(17)$ Å $\alpha = 95.068(4)°$ $b = 12.126(3)$ Å $\beta = 102.203(4)°$ $c = 13.051(3)$ Å $\gamma = 94.498(4)°$
Volume	1380.0(14) Å^3	1174.9(4) Å^3
Z	4	2
Density (calculated)	2.308 mg/m^3	2.093 mg/m^3
Absorption coefficient	12.518 mm^{-1}	7.387 mm^{-1}
F(000)	888	711
Crystal size	$0.50 \times 0.20 \times 0.20$ mm^3	$0.3 \times 0.3 \times 0.3$ mm^3
θ range for data collection	4.00 to 30.06°	2.21 to 31.07°
Index ranges	$0 \Leftarrow h \Leftarrow 24$, $0 \Leftarrow k \Leftarrow 16$, $9 \Leftarrow l \Leftarrow 9$	$-11 \Leftarrow h \Leftarrow 11, -17 \Leftarrow k \Leftarrow 17$, $-18 \Leftarrow l \Leftarrow 18$
Reflections collected	2043	14393
Independent reflections	1986 [*R*(int) = 0.0407]	7125 [*R*(int) = 0.0270]
Completeness to $\theta = 28.06°$	98.1%	94.8%
Absorption correction	Psi-scan	Semi-empirical from equivalents
Max. and min. transmission	0.1886 and 0.0621	0.86 and 0.51
Refinement method	Full-matrix least squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	1986/0/87	7125/0/434
Goodness of fit on F^2	0.975	1.028
Final *R* indices [for 4364 rflns with $I > 2\sigma(I)$]	$R1 = 0.0247$, $wR2 = 0.0587$	$R1 = 0.0275$, $wR2 = 0.0661$
R indices (all data)	$R1 = 0.0382$, $wR2 = 0.0599$	$R1 = 0.0312$, $wR2 = 0.067$
Largest diff. peak and hole	1.154 and −1.710 eA^{-3}	2.632 and −2.114 e A^{-3}

TABLE II Selected bond lengths and angles for the [Pb$(phen)_2(NO_3)_{0.7}(ClO_4)_{0.3}$]($ClO_4$)

Bond lengths (Å)		*Bond angles* (°)	
Pb(1)–N(2)	2.443(3)	N(2)–Pb(1)–N(4)	66.32(8)
Pb(1)–N(1)	2.531(3)	N(2)–Pb(1)–N(1)	76.52(13)
Pb(1)–N(1)	2.544(3)	N(4)–Pb(1)–N(1)	85.05(9)
Pb(1)–N(3)	2.552(3)	N(2)–Pb(1)–N(3)	85.49(9)
Pb(1)–O(8)	2.643(3)	N(4)–Pb(1)–N(3)	65.02(9)
Pb(1)–O(9)	2.752(3)	N(1)–Pb(1)–N(3)	142.82(9)
		N(2)–Pb(1)–O(8)	74.54(9)
		N(4)–Pb(1)–O(8)	132.77(8)
		N(1)–Pb(1)–O(8)	116.84(8)
		O(2)–Pb(1)–O(4)	74.96(9)
		N(3)–Pb(1)–O(8)	45.30(12)
		N(2)–Pb(1)–O(9)	74.19(10)
		N(4)–Pb(1)–O(9)	150.32(9)
		N(1)–Pb(1)–O(9)	74.07(9)
		N(3)–Pb(1)–O(9)	122.54(9)
		O(8)–Pb(1)–O(9)	48.08(8)

isotopic thermal parameter. R, R_w, with goodness of fit on F^2 0.975 and 1.028 are 0.0247, 0.0587 and 0.0275, 0.0661 for $[Pb(bpy)(SCN)_2]$ and $[Pb(phen)_2(NO_3)_{0.7}$-$(ClO_4)_{0.3}]$ (ClO_4), respectively. The final difference density map showed a maximum peak and hole of 1.154, $-1.710\,e\text{Å}^{-3}$ for $[Pb(bpy)(SCN)_2]$ and 2.632, $-2.114\,e\text{Å}^{-3}$ for $[Pb(phen)_2$ $(NO_3)_{0.7}(ClO_4)_{0.3}](ClO_4]$. Corrections for the Lorentz and polarization effects as well as the empirical correction for absorption using the psi-scans programs were applied. All structural calculations were carried out with a PDP-11/23+ computer using the SDP-PLUS program package [30,31].

Crystal data and structure refinement are given in Table I. Selected bond lengths and angles are given in Tables II and III. Anisotropic 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. 1–4.

TABLE III Selected bond lengths and angles for the $[Pb(bpy)(SCN)_2]$

Bond lengths (Å)		*Bond angles* (°)	
Pb(1)–N(2)	2.652(5)	N(1)–Pb(1)–N(1) #1	65.01(17)
Pb(1)–N(1)	2.517(4)	N(2)–Pb(1)–N(1)	71.87(13)
Pb(1)–N(2)#1	2.652(5)	N(1) #1–Pb(1)–N(2)	87.66(14)
Pb(1)–N(1) #1	2.517(4)	N(1)–Pb(1)–N(2) #1	87.66(14)
		N(2)–Pb(1)–N(2) #1	155.91(19)
		N(1) #1–Pb(1)–N(2)#1	71.87(13)

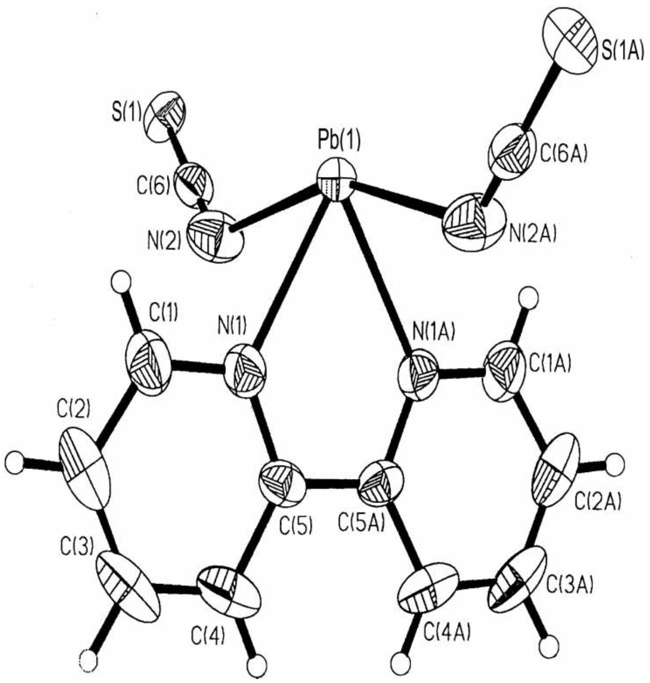

FIGURE 1 ORTEP diagram of the $[Pb(bpy)(NCS)_2]$ molecule.

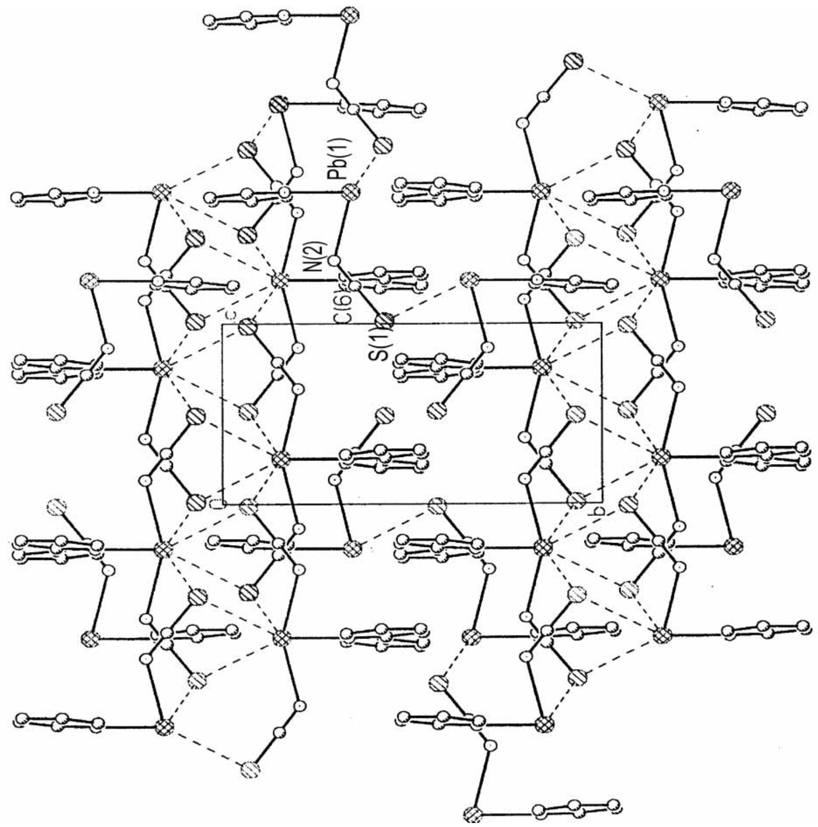

FIGURE 2 Perspective view showing the chain structure and coordination environment of $[Pb(bpy)(NCS)_2]$

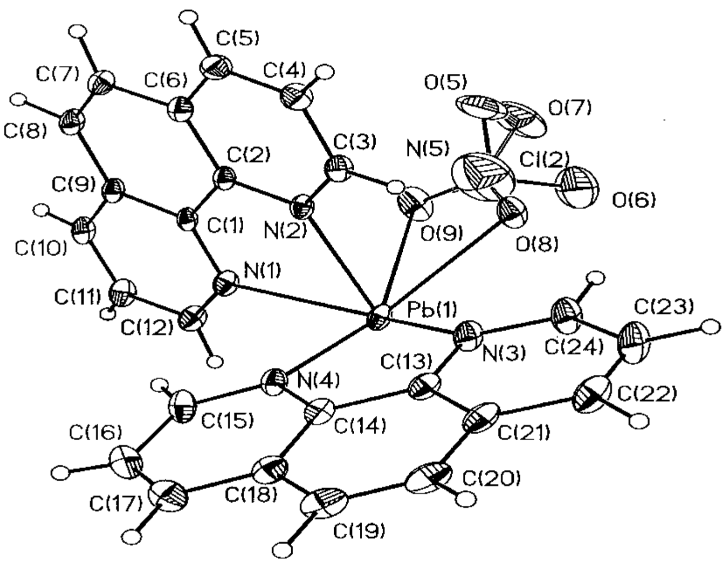

FIGURE 3 ORTEP diagram of the $[Pb(phen)_2(NO_3)_{0.7}(ClO_4)_{0.3}](ClO_4)$ molecule.

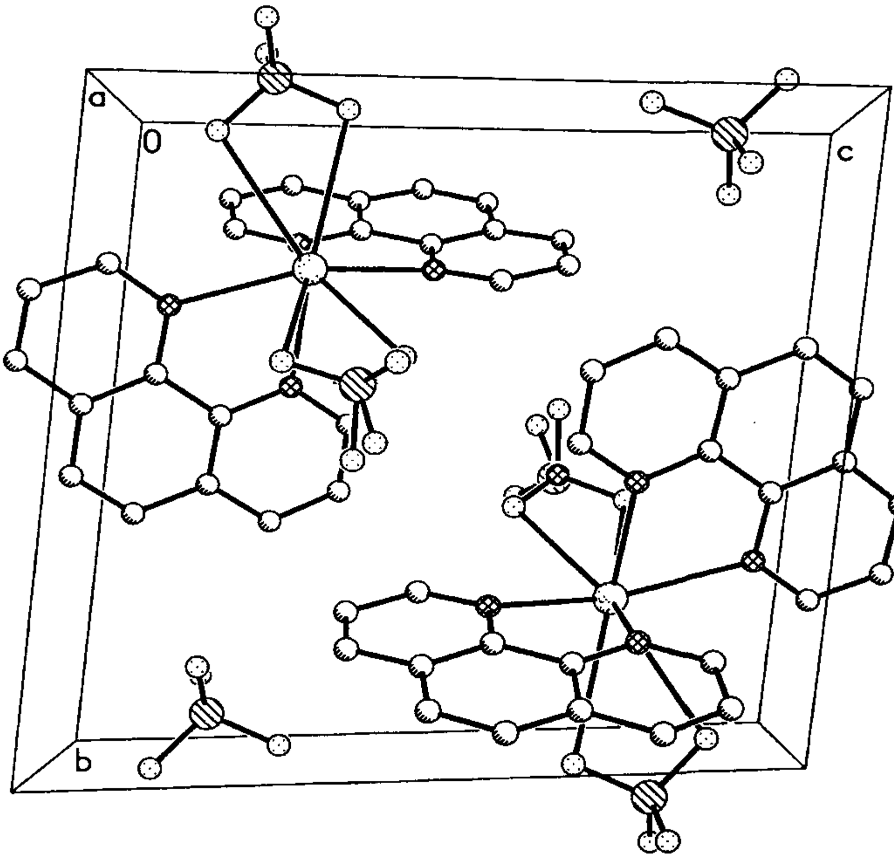

FIGURE 4 The unit cell of the $[Pb(phen)_2(NO_3)_{0.7}(ClO_4)_{0.3}](ClO_4)$.

RESULTS AND DISCUSSION

Synthesis

The reactions between $Pb(NO_3)_2$ with 1,10-phenanthroline (phen) and sodium perchlorate, $Pb(NO_3)_2$ with 1,10-phenanthroline (phen) and potassium thiocyanate, $Pb(ClO_4)_2$ with 1,10-phenanthroline (phen) and potassium thiocyanate, and $Pb(NO_3)_2$ with 2,2′-bipyridine (bpy) and potassium thiocyanate by diffusion along a thermal gradient in methanol solution (the branched tube method), provided powdery materials analyzing as $[Pb(phen)_2(NO_3)(ClO_4)]$, $[Pb(phen)_2(SCN)(ClO_4)]$, $[Pb(phen)_2(NO_3)(SCN)]$, and $[Pb(bpy)(SCN)_2]$,

The IR spectrum of the $[Pb(phen)_2(NO_3)(ClO_4)]$ shows $\nu(NO_3)$ at *ca.* 1380 cm^{-1}, and $\nu(ClO_4)$ at *ca.* 1090 cm^{-1} and $[Pb(bpy)(SCN)_2]$ complex show $\nu(SCN)$ at *ca.* 2040 cm^{-1}. The IR spectrum of the $Pb(phen)_2(SCN)(NO_3)$ shows $\nu(NO_3)$ at *ca.* 1378 cm^{-1}, and $\nu(SCN)$ at *ca.* 2045 cm^{-1} and $Pb(phen)_2(SCN)(ClO_4)$ shows $\nu(SCN)$ at *ca.* 2020 cm^{-1}, and $\nu(ClO_4)$ at *ca.* 1070 cm^{-1}.

The isolation of a suitable single crystal of the $Pb(phen)_2(SCN)(ClO_4)$ complex for X-ray crystallography was not successful and each time a powdery compound was isolated. Attempts to grow single crystals of $Pb(phen)_2(NO_3)(ClO_4)$ from water for X-ray crystallographic study gave white crystals that analytical data indicated $[Pb(phen)_2(NO_3)_{0.7}(ClO_4)_{0.3}](ClO_4)$, as was subsequently confirmed by a crystallographic study.

An interesting point is that we tried to isolate the mixed-anions complexes of the 2,2′-bipyridine ligand with Pb(II) ion, but these attempts were not successful.

Crystal Structure of $[Pb(bpy)(SCN)_2]$

An molecular structure consists of polymeric, with various similarities to polymeric $(phen)Pb(SCN)_2$ [32], $PbI_2(L)$ (L = 2,2′-bipyridine, and 1,10-phenanthroline) [33], and $Cu(bpy)(SCN)_2$ [34], in which the lead atoms are eight-coordinate, PbN_4S_4: two of the coordinated sites are occupied by the nitrogen atoms of bidentate bipyridine, the four nitrogen atoms are clustered about one pole of the symmetry axis, with the four sulfur atoms about its opposite and rather long (Pb–S = 3.25–3.46 Å). The arrangement of two SCN^- anions suggests a gap in coordination geometry around the metal ion (angle N(2)–Pb(1)–N(2A) is 155.91(19)), occupied possibly by a stereoactive lone pair of electrons on the lead(II) [14]. The observed shortening of the Pb–N bond on the side of the Pb (II) ion opposite to the position of the putative lone pair [2.517(4) compared with 2.652(5) Å adjacent to lone pair] supports the presence this feature [35]. Hence, the geometry of the nearest coordination environment of every lead atom is likely caused by the geometrical constraints of coordinated 2,2′-bipyridine and two SCN^- anions and also by the influence of a stereochemically active lone pair of electrons in a hybrid orbital on the metal atom occuping one equatorial coordination site of a *pseudo*-trigonal bipyramid. Such an environment leaves space for bonding of sulfur atoms.

Crystal Structure of $[Pb(phen)_2(NO_3)_{0.7}(ClO_4)_{0.3}](ClO_4)$

An attempt to isolate single crystals of $Pb(phen)_2(NO_3)(ClO_4)$ from water led to the isolation of $[Pb(phen)_2(NO_3)_{0.7}(ClO_4)_{0.3}](ClO_4)$ in which there are two independent ClO_4^- anions, one not coordinated to lead but another sharing a position with NO_3^-. The crystallographic analysis shows that 30% of these positions are occupied by ClO_4^- anions and 70% by NO_3^- anions that are coordinated to lead in a bidentate fashion. The Pb atom lies in a unsymmetrical six-coordinate, N_4O_2 (four by nitrogen atoms of two 1,10-phenanthroline ligands and two oxygen atoms of $[(ClO_4)_{0.3}(NO_3)_{0.7}]$ anions). Determination of the structure of this complex by X-ray crystallography showed the complex in the solid state (Fig. 1) to be a monomeric species, unlike polymeric $Pb(phen)(CH_3COO)(ClO_4)$ and $Pb(phen)(CH_3COO)(NO_3)$. The arrangement of two 1,10-phenanthroline ligands and the $[(ClO_4)_{0.3}(NO_3)_{0.7}]$ anion suggest a gap or hole in the coordination geometry around the metal ion, occupied possibly by a stereoactive lone pair of electrons on lead (II). The observed shortening of the Pb–N and Pb–O bonds on the side of the Pb(II) ion opposite to the position of the putative lone pair (2.443 Å compared with 2.531, 2.544, 2.552 and 2.643 Å compared with 2.752 Å adjacent to the lone pair) (Table II) supports the presence the lone pair [35].

Stereochemical activity of the lone pair in divalent lead compounds has recently been discussed by Shimoni-Livny *et al.* based on a thorough review of crystal data available in the Cambridge Structural Database (CSD) [36]. Lead complex coordination is classified as holo-directed or hemi-directed. Holo-directed refers to complexes in which the bonds to ligand atoms are directed throughout the surface of an encompassing sphere, while hemi-directed refer to those cases in which the bonds to ligand atoms are directed throughout only part of coordination sphere, leaving a void or gap in the distribution of bonds to the ligand. The latter is observed in all Pb(II) compounds with coordination numbers 2 to 5, quite common in Pb(II) complexes with coordination numbers 6, 7 and 8, and does not exist in lead complexes with higher coordination numbers, where holo-directed geometry is observed. For the structures described here, coordination around the lead atoms is hemi-directed with a significant gap *trans* to the chelating 1,10-phenanthroline and 2,2′-bipyridine ligands.

The strikingly different feature of $[Pb(bpy)(SCN)_2]_n$ compared to $[Pb(phen)_2(NO_3)_{0.7}(ClO_4)_{0.3}](ClO_4)$ is that there is a π–π stacking [37,38] interaction (charge-transfer arrays) between the parallel aromatic rings belonging to adjacent chains in the $[Pb(bpy)(SCN)_2]_n$ compound, as shown in Fig. 2. Do the π–π stacking interactions between the parallel aromatic rings help to increase the "gap" in coordination geometry around the metal ion or does the "gap" arising from the "stereochemical activity" of valence shell lone electron pairs help to form π–π stacking? The "gap" in $[Pb(phen)(SCN)_2]_n$ [33], $[Pb(bpy)Br_2]_n$ and $[Pb(bpy)I_2]_n$ [9] is larger than in $[(phen)_2Pb(NO_3)_2]$ [9], and $[(phen)_2Pb(ClO_4)_2]$ [9]. Such π–π stacking interactions are rarely observed in complexes with the ratio of ligand–metal 2 : 1. In both 1 : 1 and 2 : 1 ratios there is a gap which is greater in the 1 : 1 than in the 1 : 2 ratio. It may be that the increased gap influences π–π stacking of aromatic units in these cases.

Acknowledgments

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Supplementary Material

Complete bond lengths and angles, coordinates and displacement parameters have been deposited at Cambridge Crystallography Data Centre. Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number 175805 for $Pb(bpy)(SCN)_2$ and 162627 for $[Pb(phen)_2(NO_3)_{0.7}(ClO_4)_{0.3}](ClO_4)$.

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