Two-Dimensional Holo- and Hemidirected Lead(II) Coordination Polymers: Synthetic, Spectroscopic, Thermal, and Structural Studies of $[Pb(\mu\text{-}SCN)_2(\mu\text{-ebp})_{1.5}]_n$ and $\{[Pb(\mu\text{-}OAc)(\mu\text{-ebp})](ClO_4)\}_n$ (ebp = 4,4′-[(1*E*)-Ethane-1,2-diyl]bis[pyridine]; OAc = Acetato)

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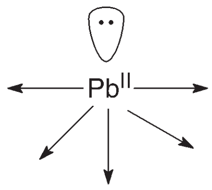
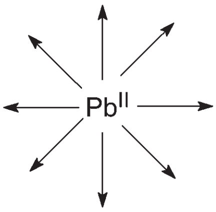
Two new coordination polymers of Pb^{II} complexes with bridging 4,4′-[(1*E*)-ethane-1,2-diyl]bis[pyridine] (ebp), thiocyanato, and acetato ligands, $[Pb(\mu\text{-}SCN)_2(\mu\text{-ebp})_{1.5}]_n$ (**1**) and $\{[Pb(\mu\text{-}OAc)(\mu\text{-ebp})](ClO_4)\}_n$ (**2**), were synthesized and characterized by elemental analysis, FT-IR, ^1H- and ^{13}C-NMR, thermal analysis, and single-crystal X-ray diffraction. In **1**, the Pb^{2+} ions are doubly bridged by both the ebp and the SCN^- ligands into a two-dimensional polymeric network. The seven-coordinate geometry around the Pb^{2+} ion in **1** is a distorted monocapped trigonal prism, in which the Pb^{2+} ions have a less-common holodirected geometry. In **2**, the Pb^{2+} ions are bridged by AcO^- ligands forming linear chains, which are also further bridged by the neutral ebp ligands into a two-dimensional polymeric framework. The Pb^{2+} ions have a five-coordinate geometry with two N-atoms from two ebp ligands and three O-atoms of AcO^-. Although ClO_4^- acts as a counter-ion, it also makes weak interactions with the Pb^{2+} center. The arrangement of the ligands in **2** exhibits hemidirected geometry, and the coordination gap around the Pb^{2+} ion is possibly occupied by a configurationally active lone pair of electrons.

Introduction. – Crystal engineering of metallo-organic frameworks has been of great interest due to the preparation of new coordination polymers exhibiting specific topologies [1]. It is possible to build crystalline metal complexes in one, two, or three dimensions, and the key factor for the design of such metal complexes is to use polyfunctional ligands capable to bridge metal centers to form polymeric structures [2]. The construction of coordination polymers has achieved great progress in forming interesting architectures with novel properties such as magnetism [3], electrical conductivity [4], nonlinear optical behavior [5], luminescence [6], and porosity [7].

Pb^{II} Complexes are frequently discussed with respect to the coordination and configurational activity of heavy metals with valence-shell-electron lone pairs [8], which are responsible for coordination-sphere distortions. The possible configurational activity of the lone pair in divalent Pb^{II} compounds has recently been discussed by *Shimoni-Livny et al.* [9], based on the crystal data available in the *Cambridge Structural Database*. These authors classified the lead coordination geometry as 'holodirected', when the bonds to ligand atoms are directed throughout the surface of an encompassing sphere, and as 'hemidirected' in cases where the bonds are directed



hemidirected



holodirected

throughout only a part of the coordination sphere, leaving a gap in the distribution of bonds to the ligands.

The 4,4′-[(1*E*)-ethane-1,2-diyl]bis[pyridine] (ebp) ligand is known to form polynuclear complexes with transition metals [10] and may also be a good candidate as a bridging ligand for the investigation of the configurational activity of valence-shell electron lone pairs in Pb^{II}. Moreover, the architectures of coordination polymers or supramolecular compounds constructed from Pb^{II} ions and the ebp ligand have not been reported so far. In this paper, we report the preparations and crystal structures of two new Pb^{II} coordination polymers, namely $[Pb(\mu\text{-}SCN)_2(\mu\text{-}ebp)_{1.5}]_n$ (**1**) and $\{[Pb(\mu\text{-}OAc)(\mu\text{-}ebp)](ClO_4)\}_n$ (**2**), involving the spontaneous aggregation of two bridging ligands, ebp and thiocyanato (SCN^-) in **1** and ebp and acetato (AcO^-) in **2**.

Results. – The IR spectra of **1** and **2** display characteristic absorption bands for ebp, SCN^- and AcO^- ligands. The relatively weak absorption bands at *ca.* 2900 and 3050 cm^{-1} are due to the C–H modes involving the ring and ethene H-atoms. In the IR spectrum of **1**, very strong bands centered at 2025 and 814 cm^{-1} characterize the $\tilde{\nu}(CN)$ and $\tilde{\nu}(CS)$ vibrations of the bridging SCN-group, respectively, while the sharp band at 536 cm^{-1} is attributed to the $\delta(SCN)$ vibration [11]. The bridging [M–SCN–M] complexes with divalent transition-metal ions is expected to show $\tilde{\nu}(CN)$ above 2100 cm^{-1} [11], but the significantly lower frequency for the $\tilde{\nu}(CN)$ vibration of **1** may be due to the presence of Pb^{II} with a relatively large ionic radius relative to that of transition metals. However, the $\nu(CN)$ frequency of **1** is comparable to those observed in the corresponding Pb^{II} polymers containing thiocyanate [12]. The absorption bands with variable intensity in the frequency range 1407–1587 cm^{-1} correspond to ring vibrations of the pyridine moiety of the ebp ligand. The IR spectrum of **2** presents strong absorption bands at 615, 1079, and 1100 cm^{-1} for the vibrations of the ClO_4^- anion. The symmetric and asymmetric vibrations of the COO^- group are observed at 1479 and 1592 cm^{-1} as sharp absorption bands, respectively. The $\Delta(\nu_{asym} - \nu_{sym})$ value of 113 cm^{-1} indicates that the AcO^- anions coordinate to the Pb^{II} centers in a bridging mode [13].

The thermal-decomposition behavior of both **1** and **2** was investigated in flowing N_2 and under a static air atmosphere. It was shown that each complex exhibits similar decomposition pathways under both N_2 and air. Compound **1** does not melt and is stable up to 205°, at which temperature it begins to decompose. Removal of the ebp ligands takes place between 205 and 500° with an endothermic effect at 272° and two exothermic effects at 335 and 468°. The experimental mass loss of 46.1% is consistent with the calculated value 45.8% for the elimination of 1.5 mol of ebp. The solid residue formed at *ca.* 500° is suggested to be $Pb(SCN)_2$, based on the IR spectrum of this residue showing characteristic absorption peaks of the thiocyanate anion at *ca.* 2100 cm^{-1}. At higher temperatures, evaporation or decomposition of the residue occurs. Compound **2** is stable up to 250° and decomposes with a continuous weight loss. Due to the presence of the ClO_4^- anion, **2** was found to be highly explosive in both N_2 and air and two peaks at 350 and 370° of violently exothermic reactions arise from the explosion of the compound, leaving an empty crucible. The thermal observations suggest that **2** may be a good candidate for energetic materials.

A view of the coordination environment around the Pb^{2+} ion in **1** is shown in *Fig. 1*, and *Table 1* lists selected bond distances and angles. Single-crystal X-ray-diffraction analysis reveals that the Pb^{2+} ion of **1** is coordinated by four SCN^{-1} and three neutral ebp molecules, resulting in a seven-coordinate complex with a PbN_5S_2 chromophore. Although the coordination geometry around the Pb^{2+} ion is irregular, presumably associated with the steric constraints arising from the shape of the present ligands, it is

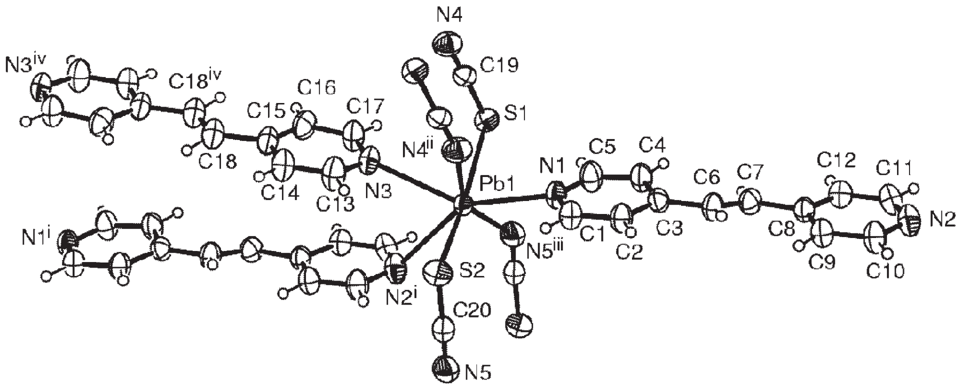


Fig. 1. *View of the coordination environment around lead(II) in* **1** *with atom-labeling scheme and thermal ellipsoids at the 40% probability level* (small spheres for the H-atoms). Symmetry codes: $i = x-1, 1+y, z$; $ii = -x, 1-y, 1-z$; $iii = -x, 1-y, -z$; $iv = -1-x, 2-y, 1-z$.

Table 1. *Selected Geometric Data for* **1**. For symmetry codes *i–iii*, see *Footnotes a–c*.

Length [Å]		Angles [°]		Angles [°]	
Pb(1)–S(1)	2.900(2)	N(1)–Pb(1)–S(1)	83.44(13)	N(3)–Pb(1)–S(1)	80.82(13)
Pb(1)–S(2)	3.062(2)	N(1)–Pb(1)–S(2)	91.04(13)	N(3)–Pb(1)–S(2)	94.27(13)
Pb(1)–N(1)	2.612(5)	N(1)–Pb(1)–N(2)[a])	143.91(11)	N(3)–Pb(1)–N(4)[b])	74.42(11)
Pb(1)–N(2)[a])	2.966(7)	N(1)–Pb(1)–N(3)	145.60(12)	N(3)–Pb(1)–N(5)[c])	122.79(10)
Pb(1)–N(3)	2.801(4)	N(1)–Pb(1)–N(4)[b])	75.62(19)	N(4)[b])–Pb(1)–S(1)	91.22(16)
Pb(1)–N(4)[b])	2.540(6)	N(1)–Pb(1)–N(5)[c])	79.79(18)	N(4)[a])–Pb(1)–S(2)	70.24(16)
Pb(1)–N(5)[c])	2.785(7)	N(2)[a])–Pb(1)–S(1)	109.20(16)	N(4)[b])–Pb(1)–N(5)[c])	151.2(2)
		N(2)[a])–Pb(1)–S(2)	85.58(16)	N(5)[c])–Pb(1)–S(1)	71.12(15)
		N(2)[a])–Pb(1)–N(3)	70.46(16)	N(5)[c])–Pb(1)–S(2)	125.40(16)
		N(2)[a])–Pb(1)–N(4)[b])	135.22(16)	S(1)–Pb(1)–S(2)	161.44(5)
		N(2)[a])–Pb(1)–N(5)[c])	73.25(16)		

[a]) $i = x-1, 1+y, z$. [b]) $ii = -x, 1-y, 1-z$. [c]) $iii = -x, 1-y, -z$.

best described as a distorted monocapped trigonal prism. The S(1)−Pb(1)−S(2) and N(4)^{ii}−Pb(1)−N(5)^{iii} bonds with SCN$^-$ form the equatorial plane (for symmetry codes *ii* and *iii*, see *Table 1*), and their bond angles are 161.44(5) and 151.2(2)°, respectively, while the N(1) atom occupies the axial position and the N(2) and N(3) atoms are placed in the pseudoaxial positions as shown in *Fig. 1*.

Complex **1** is a two-dimensional neutral metallopolymer as illustrated in *Fig. 2*. The complex crystallizes in the triclinic space group *P*−1 and consists of the Pb^{2+} ions bridged by both ebp and SCN$^-$ ligands, thus forming a two-dimensional, infinite framework. On the other hand, the structure may be considered a coordination polymer of Pb^{II} consisting of one-dimensional linear chains, running parallel to the *c* axis, with a building block of [Pb(SCN)$_2$]. Two SCN$^-$ anions doubly bridge two Pb^{2+} ions *via* the N and S atoms with bond distances Pb(1)−S(1) = 2.900(2) Å, Pb(1)−S(2) = 3.062(2) Å, Pb(1)−N(4)^{ii} = 2.540(6) Å and Pb(1)−N(5)^{iii} = 2.785(7) Å. The two Pb−S bond distances in **1** are practically similar, but significantly shorter than those found in the reported Pb^{2+} complexes with thiocyanate [12]. The intrachain Pb···Pb distances

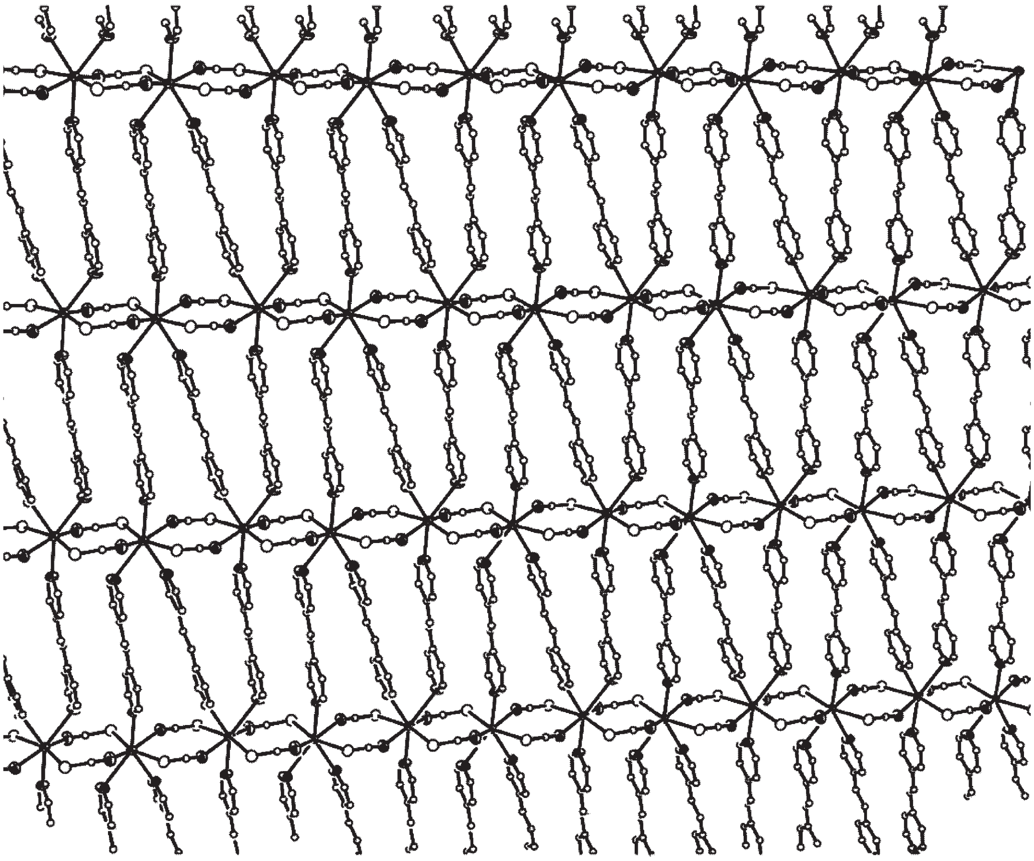


Fig. 2. *Fragment of the two-dimensional framework in* **1** *viewed along the* a*-axis.* H-Atoms of CH groups are omitted for clarity.

within the $[Pb(SCN)_2]_n$ chains are 5.291 and 6.149 Å. The individual polymeric chains are almost parallel to each other and further bridged by bidentate bridging ebp ligands, with bond distances Pb(1)−N(1) = 2.612(5) Å, Pb(1)−N(2)^i = 2.966(7) Å and Pb(1)−N(3) = 2.801(4) Å, resulting in a two-dimensional framework, as shown in *Fig. 2* (for symmetry code *i*, see *Table 1*). The Pb(1)−N(2)^i and Pb(1)−N(3) bond distances are significantly longer than the third Pb−N (ebp) bond, and the lengthening of the Pb−N(ebp) bonds is explained by the poor overlap of the sp^3 lone pair on the N-atoms of ebp with the valence orbitals of the adjacent Pb^{2+} ion, due to steric constrains.

The two pyridine rings of the ebp ligand are essentially planar with an r.m.s. deviation of *ca.* 0.035 Å. However, atoms C(6) and C(7) are displaced from the pyridine best planes by 0.043(4) and 0.339(4) Å, respectively. The C(18) atom and its symmetry equivalent partner also deviate by the same amount as atoms C(6) and C(7). Since the inversion center is located at the middle of the C(18)−C(18)^{iv} bond (symmetry code $iv = -1-x, 2-y, 1-z$], the aromatic rings of the ebp ligand are suppose to be coplanar, and the whole ebp molecule may be considered flat, because the dihedral angle between the two pyridine rings within the ebp ligand is only 2.40(3)°.

The structure of **1** does not exhibit conventional H-bonds. In the crystal packing, the two-dimensional layers are shifted against each other by half of the distance between two Pb^{2+} centers connected by the ebp ligands, and are held together by aromatic $\pi-\pi$ stacking interactions between the pyridine fragments of the ebp ligands in the adjacent layers, with average centroid–centroid distances of 3.68(5) Å.

The fundamental building unit of the crystal structure of **2** is shown in *Fig. 3*, and selected bond lengths and angles are listed in *Table 2*. Complex **2** crystallizes in the orthorhombic space group $Pna2_1$. The structure consists of $[Pb(\mu\text{-OAc})(\mu\text{-ebp})]^+$ cations and ClO_4^- anions. Some of the O atoms (C2–C4) of the ClO_4^- anion are disordered over two positions with essentially equal occupancy. The complex cation is a

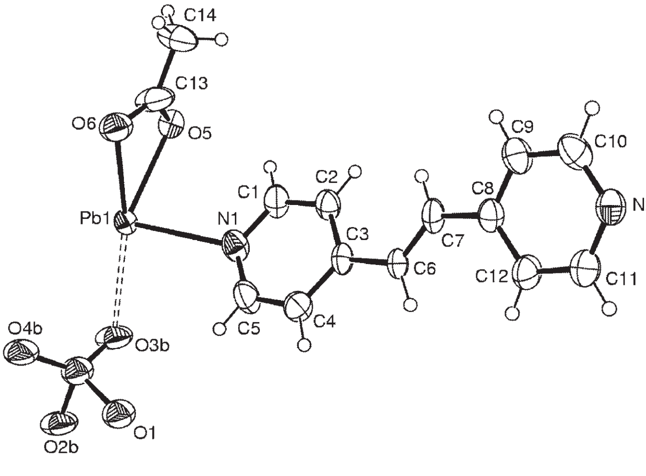


Fig. 3. *Molecular view of the building-block unit in* **2** *with atom-labeling scheme and thermal ellipsoids at the 40% probability level* (small spheres for the H-atoms)

Table 2. *Selected Geometric Data for* **2**. For symmetry codes *i – v*, see *Footnotes a – e*.

	Length [Å]		Angle [°]		Angle [°]
Pb(1)–N(1)	2.646(13)	O(5)–Pb(1)–O(6)	50.3(3)	O(6)–Pb(1)–N(1)	91.2(5)
Pb(1)–N(2)[a])	2.606(10)	O(5)–Pb(1)–O(6)[b])	69.3(3)	O(6)–Pb(1)–N(2)[a])	90.4(4)
Pb(1)–O(5)	2.464(8)	O(5)–Pb(1)–N(1)	80.1(4)	O(6)[b])–Pb(1)–N(1)	82.1(5)
Pb(1)–O(6)	2.579(8)	O(5)–Pb(1)–N(2)[a])	81.4(3)	O(6)[b])–Pb(1)–N(2)[a])	74.9(5)
Pb(1)–O(6)[b])	2.471(10)	O(6)–Pb(1)–O(6)[b])	119.4(3)	N(1)–Pb(1)–N(2)[a])	154.4(4)
Pb(1)–O(3)b	2.938(7)				
Pb(1)–O(5)[c])	2.962(8)				

D–H···A	*d*(D–H) [Å]	*d*(H···A) [Å]	*d*(D···A) [Å]	< (D–H···A) [°]
C(1)–H(1)···O(5)	0.93	2.52	3.17(2)	126
C(5)–H(5)···O(3)a	0.93	2.50	3.36(5)	154
C(2)–H(2)···O(2)b[d])	0.93	2.56	3.20(2)	127
C(4)–H(4)···O(4)b[e])	0.93	2.36	3.19(6)	148
C(9)–H(9)···O(1)[d])	0.93	2.50	3.35(2)	151

[a]) *i* = *x* – 1/2, *y* – 1/2, 1/2 + *z*. [b]) *ii* = *x* – 1/2, 1/2 – *y*, *z*. [c]) *iii* = 1/2 + *x*, 1/2 – *y*, *z*. [d]) *iv* = 1/2 – *x*, *y* – 1/2, 1/2 + *z*. [e]) *v* = 1 – *x*, 1 – *y*, 1/2 + *z*.

two-dimensional framework, in which Pb^{2+} ions are bridged by both AcO$^-$ and ebp ligands as illustrated in *Fig. 4*. The COO$^-$ moiety of the AcO$^-$ ligand act as both bidentate and bridging group (totally tridentate) in a μ-1,3 mode, where the two O-atoms of the COO$^-$ group bidentately coordinate to a Pb^{2+} ion, creating a four-membered chelate ring, and one of them also bridges two adjacent Pb^{2+} ions, yielding a one-dimensional chain. The intrachain distance between two neighboring Pb^{2+} ions is 4.312 Å. These one-dimensional chains running parallel to the *a* axis are further linked by the ebp ligands, which behave as bidentate bridging ligands *via* two N-atoms, thus creating a two-dimensional coordination polymer as shown in *Fig. 4*.

The Pb^{2+} ions in **2** are five-coordinate of the PbO$_3$N$_2$ type. The calculated structural index parameter τ value of 0.57 reflects a significantly distorted trigonal-bipyramidal geometry since the τ values of square-based-pyramidal and trigonal-bipyramidal extremes are 0 and 1, respectively [14]. The best equatorial trigonal plane is defined by atoms O(6)^{ii}, Pb(1), O(6), and O(5) with a torsion angle of – 4.7°, while the N(1) and N(2) atoms occupy the axial positions (N(1)–Pb(1)–N(2)^{i} = 154.4(4)°) (for symmetry codes, see *Table 2*). The large distortion in the coordination polyhedron of **2** may be the consequence of a very small bite angle (50.3(3)°) of the AcO$^-$ ligand, which is similar to that found in [Pb(H$_2$O)(OAc)(sac)]$_n$ (sac = saccharinato) [15].

The Pb–N distances of 2.606(10) and 2.646(13) Å are significantly shorter in **2** than the corresponding distances in **1**. The Pb–O(bidentate AcO) distances are 2.464(8) and 2.579(8) Å, while the Pb–O(bridging AcO) distance is 2.471(10) Å. The Pb–O(AcO) distances are significantly different from those reported for [Pb(en)(OAc)(NO$_3$)]$_n$ [44], [Pb(phen)(OAc)(ClO$_4$)]$_n$ [16], [Pb(phen)(OAc)(NO$_3$)] [17], [Pb(bpy)(OAc)(ClO$_4$)] [18], [Pb(phen)(OAc)$_2$]$_2$ · 4 H$_2$O [19] and [Pb(dpa)$_2$(OAc)$_2$]$_n$ [20] (en = ethane-1,2-diamine, phen = 1,10-phenanthroline, dpa = di(pyridin-2-yl)amine). There are also weak interactions of Pb^{2+} with the O(5) atom of adjacent AcO$^-$ anions (Pb ··· O(5)^{iii} = 2.962(8) Å) and the O(3) atom of the ClO$_4^-$ anion (Pb ··· O(3b) = 2.938(7) Å).

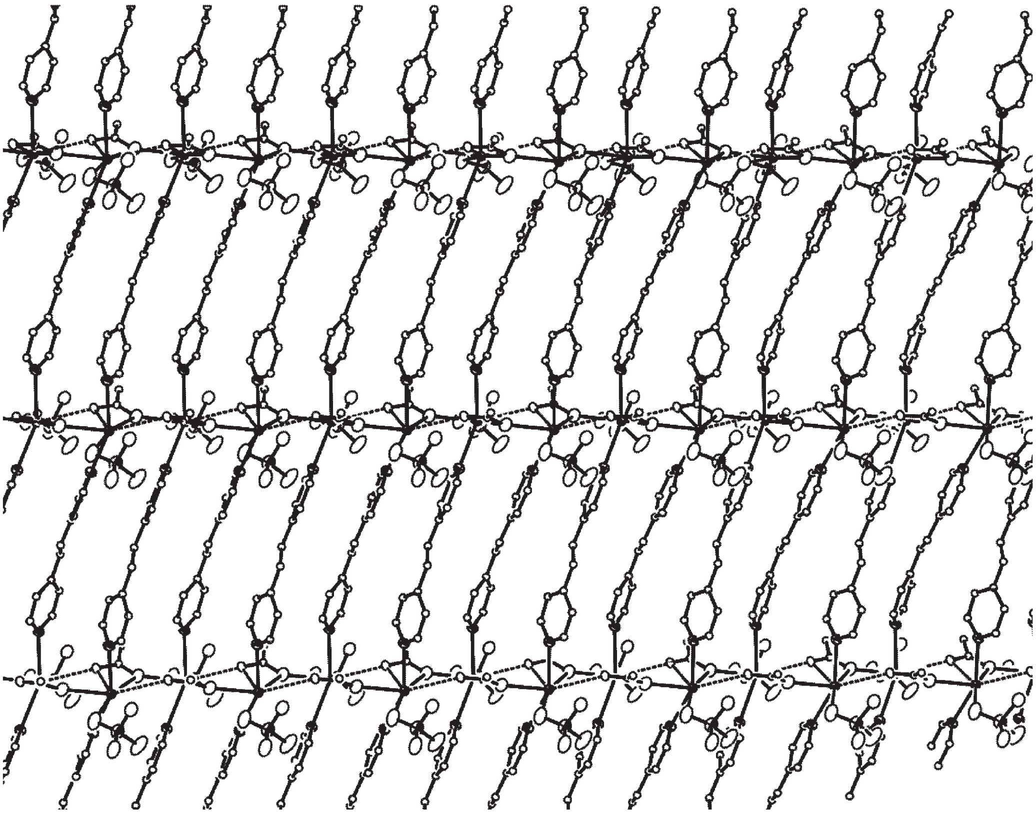


Fig. 4. *Fragment of the two-dimensional layer in* **2** *viewed along the* b-*axis.* H-Atoms of CH groups are omitted for clarity, and dashed lines indicate weak interactions of Pb^{III} with some O-atoms of the AcO ligands and ClO_4^- anions.

The pyridine rings of the ebp ligand, (C(1) to C(5), and N(1)) and (C(8) to C(10), and N(2)) are essentially planar with r.m.s. deviations of *ca.* 0.010 Å. In contrast to **1**, the ebp ligand in **2** is not flat, since the dihedral angle between the two pyridine rings is 27.23(5)°. The two- dimensional layers of **2** are held together by aromatic $\pi-\pi$ stacking interactions of *ca.* 3.72(2) Å and weak $CH\cdots O$ interactions as listed in *Table 2.*

Discussion. – Pb^{II} Complexes **1** and **2**, two new two-dimensional coordination polymers, were prepared by the branch-tube method and structurally characterized. Their crystal structures are consistent with the results obtained from the physical-characterization measurements. Complexes **1** and **2** are the first two-dimensional Pb^{II} frameworks with the bridging ebp ligand. In addition to ebp, **1** contains bridging SCN^- ions, whereas **2** is a mixed-anion compound with bridging AcO^- ions and ClO_4^- as counter-ion.

It is very interesting to note that, although **1** and **2** show similar polymeric networks, their Pb^{2+} ions exhibit different coordination geometries. *Shimoni-Livny et al.* [9] stated that hemidirected geometry (see *Introduction*) is present in all Pb^{2+} compounds with coordination numbers as low as 2–5 and also quite common for coordination numbers 6–8, while holodirected geometry (see *Introduction*) becomes dominant at higher coordination numbers such as 9 and 10. Furthermore, holodirected geometry is also favored at the intermediate coordination numbers 6–8 in the presence of soft and bulky ligands.

The Pb^{2+} ion in **1** is seven-coordinate, and the direction of the Pb–N and Pb–S bonds shows that the coordination around the Pb^{2+} ion in this complex is holodirected. Therefore, the arrangement of ebp and SCN^- ligands do not leave any gap or hole in the coordination sphere around the Pb^{II} atom, indicating that the electron lone pair of Pb^{II} is inactive. The presence of four anionic SCN^- and three bulky ebp ligands increases steric crowding around the Pb^{II} atom and results in strong interligand repulsions. This may be the reason of the disappearance of the gap in the coordination polyhedron, thereby resulting in the less-common holodirected geometry. This is in accord with the holodirected eight-coordinate Pb^{2+} ions in $[Pb(bpy)(NO_3)(SCN)]_n$ containing the bulky 4,4′-bipyridine (bpy) ligand together with two different anionic species [8].

The Pb^{2+} ion in **2** is five-coordinate and displays hemidirected geometry with a configurationally active lone pair as expected. Additionally, the $O(6)-Pb-O(6)^{ii}$ angle of 119.4(3)° suggests that there is a hole in the coordination sphere of **2** due to lone-pair/bond-pair repulsion. The hybrid orbital containing the putative electrons lone pair is possibly located at the *trans* position to the shorter Pb–O bond, and the observed shortening of this Pb–O bond (bond distances for Pb(1)–O(5), Pb(1)–O(6) and $Pb(1)-O(6)^{ii}$ of 2.464(8), 2.579(8), and 2.471(10) Å, resp.) supports the presence of this feature [21]. It is important to note that the presence of a lone pair is not directly determined, but it is deduced from the spatial distribution of the donor atoms of ligands around the metal center. Therefore, the identification of these donors is essential for the analysis of any particular system. For example, in **2**, the coordination number of 5 was estimated assuming an upper limit of *ca.* 2.75 Å for Pb–donor atom interactions, and, therefore, a hemidirected coordination sphere was established due to the Pb–N and Pb–O bond distances ranging from 2.464(8) to 2.646(13) Å. However, if the weaker Pb–O separations over 2.9 Å are taken into consideration, the coordination number becomes 7. In this case, Pb^{II} ions in **2** are still hemidirected, because the $O(6)-Pb-O(6)^{ii}$ angle of 119.4(3)° was not influenced by the coordination of the perchlorate anion, due to occupation of this site by the configurationally active electron lone pair at the Pb^{II} atom. It may be concluded that the identification of a lone pair is not readily achieved in mixed-ligand Pb^{II} coordination polymers when relatively weak donors are present.

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Experimental Part

General. Thermal-analysis curves (TG and DTA): *Rigaku-TG8110* thermal analyzer; heating rate 10° min^{-1} in flowing N_2 or under a static air atmosphere. FT-IR Spectra: *Perkin-Elmer 597* spectrophotometer, KBr pellets; 4000–400 cm^{-1} range. NMR Spectra: *Bruker DRX-500-Avance* spectrometer, δ in ppm. Elemental analyses: *Heraeus CHN-O-Rapid Analyzer* for C, H, and N.

*Sesqui{4-[2-(pyridin-4-yl)ethyl]pyridine-κ*N*}bis(thiocyanato-κ*S*)lead Homopolymer* (*[Pb(μ-SCN)$_2$(μ-ebp)$_{1.5}$]*$_n$; **1**). The so-called 'branch-tube' method was used: ebp (0.180 g, 1 mmol) was placed in one arm of the branched tube, and mixtures of lead(II) acetate (0.36 g, 1mmol) and KSCN (1.96 g, 2 mmol) in the other. MeOH was carefully added to fill both arms. The tube was sealed and the ligand-containing arm was immersed in a bath at 60° while the other was at r.t. After 15 d, colorless crystals were collected in the cooler arm. They were filtered off, washed with acetone and Et_2O, and air-dried: **1** (45%). M.p. 205° (dec.). ^{1}H-NMR (DMSO): 7.53 (*s*, 2 H), 7.60 (*d*, 4 H): 8.60 (*d*, 4 H). ^{13}C-{^{1}H}-NMR (DMSO): 121.2; 130.6; 143.3; 150.20. Anal. calc. for $C_{20}H_{15}N_5PbS_2$: C 40.22, H 2.51, N 11.73; found: C 40.35, H 2.25, N 11.60.

*(Acetato-κ*O*,κ*O'*){4-[2-(pyridin-4-yl)ethyl]ethyl]pyridine-κ*N*}lead(1+) Perchlorate Homopolymer* (*{[Pb(μ-OAc)(μ-ebp)](ClO$_4$)}*$_n$; **2**). As described for **1**, but with $NaClO_4$ replacing KSCN. After 20 d, white crystals were deposited in the cooler arm: **2** (40%) M.p. 250° (dec). ^{1}H-NMR (DMSO): 1.729 (*s*, 3 H); 7.53 (*s*, 2 H); 7.60 (*d*, 4 H); 8.60 (*d*, 4 H). ^{13}C-{^{1}H} NMR (DMSO): 27.536 (MeCOO); 178.817 (MeCOO); 121.242, 130.567, 143.337, 150.183. Anal. calc. for $C_{14}H_{13}ClN_2O_6Pb$: C 30.69, H 2.39, N 5.11; found: C 30.80, H 2.50, N 5.30.

X-Ray Crystallography. Intensity data for **1** and **2** were collected with a *Stoe-IPDS-2* diffractometer (Mo–K_α radiation, λ 0.71073 Å) at 293(2) K. The structures were solved by direct methods and refined by full-matrix least-squares techniques on F^2. All H-atoms were placed in idealized locations and refined by riding on their carrier atoms. Crystal data of **1**: $C_{20}H_{15}N_5PbS_2$, *M* 596.71; crystal dimensions 0.33 × 0.27 × 0.20 mm; triclinic, $P-1$; $a = 9.899(2)$, $b = 9.989(2)$, $c = 11.425(2)$ Å, $\alpha = 107.910(15)$, $\beta = 104.464(16)$, $\gamma = 90.894(16)°$; $Z = 2$, $V = 1035.7(4)$ Å^3, $D_c = 1.913$ g/cm^3; $\mu = 8.361$ mm^{-1}; $F(000) = 568$, θ range = 2.14–28.66°; reflections collected (independent) = 18793 (5273), $R_1(wR_1) = 0.0399$ (0.0757). Crystal data of **2**: $C_{14}H_{13}ClN_2O_6Pb$, *M* 547.90, crystal dimensions 0.50 × 0.30 × 0.16 mm; orthorhombic, $Pna2_1$; $a = 7.4359(3)$, $b = 16.5857(11)$, $c = 13.6191(6)$ Å, $Z = 4$, $V = 1679.64(15)$ Å^3, $D_c = 2.167$ g/cm^3; $\mu = 10.236$ mm^{-1}, $F(000) = 1032$; θ range = 1.93–27.50°; reflections collected (independent) = 26548 (2013); $R_1(wR_1) = 0.0369$ (0.0940). CCDC Nos. 253686 and 248252 contain the supplementary crystallographic data for **1** and **2**, respectively. These data can be obtained free of charge from the *Cambridge Crystallographic Data Centre via* www.ccdc.cam.ac.uk/data_request/cif.

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