Holo- and Hemidirected Coordination Spheres in a Novel Three-Dimensional Polymeric $K^{I}Pb^{II}$ Heteropolynuclear Complex: X-Ray Crystal Structure of $[KPb(AcO)_2(SCN)]_n$

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A novel three-dimensional polymeric $K^{I}Pb^{II}$ heteropolynuclear complex, $[KPb(AcO)_2(SCN)]_n$, with mixed acetate and thiocyanate ligands, has been synthesized and characterized. Its single-crystal X-ray structure (*Fig. 1*) shows three types of K^+ ions with coordination numbers of seven, and three types of Pb^{2+} ions with coordination numbers of eight, eight, and nine, respectively. The Pb centers (Pb(1) and Pb(3); *Fig. 1*) with coordination numbers of nine and eight, respectively, possess stereochemically 'inactive' electron lone pairs, and the coordination sphere is *holodirected*. However, the arrangement of O-, N-, and S-atoms for the eight-coordinated Pb(2) suggests a gap or hole in the coordination geometry around this atom. This 'hole' is possibly occupied by a stereochemically 'active' electron lone pair of Pb(2), and its coordination sphere is, thus, *hemidirected*.

Introduction. – An issue frequently discussed in considering the coordination of heavy metals is the so-called 'stereochemical activity' of valence-shell electron lone pairs [1–5]. In particular, recent structural studies on Pb^{II} compounds [6][7] have provided a basis for a rather detailed analysis of coordination-sphere distortions as a consequence of the presence of such lone pairs. The possible stereochemical activity of the lone pair in divalent Pb compounds has recently been discussed by *Shimoni-Livny et al.* [7] based on a thorough review of crystal data available from the *Cambridge Structural Database* (*CSD*) and by means of *ab initio* calculations. These authors classified lead coordination 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 throughout only part of the coordination sphere, leaving a gap in the distribution of bonds to the ligand. The latter case, present in all Pb^{II} complexes with coordination numbers 2–5, is also quite common in Pb^{II} complexes with coordination numbers 6, 7, and 8, but has not been found in those with higher coordination numbers, where holodirected geometry is the rule. The lone-pair activity can also depend on *1*) hard or soft ligands, *2*) attractive or repulsive interactions among ligands, *3*) the p character of lone pairs, and *4*) the number of electrons (charge) transferred from the ligands to the metal [7].

The structures of $[Pb^{II}(SCN)_2]$ [8] and $[Pb^{II}(AcO)_2]$ [9] are known, and the lone pairs in these complexes behave differently. The solid-state structure of $[Pb^{II}(SCN)_2]$ shows Pb^{2+} to be eight-coordinated by bridging thiocyanato groups, with no apparent vacancy in the coordination sphere. Thus, the metal-ion lone pair is likely to be stereochemically 'inactive'. In contrast, $[Pb^{II}(AcO)_2]$ (trihydrate) shows a chain-like structure, with chelating and bridging acetato groups, together with coordinated H_2O, which raises the overall coordination number to eight [9]. In spite of this high coordination number, an apparent vacancy in the coordination sphere suggests stereochemical 'activity' of the Pb^{2+} lone pair. In [8][9], no specific reason had been given for this phenomenon. Probably, the inactivity of the lone pair in $[Pb(SCN)_2]$ is due to the thiocyanato S-atoms, which acts as as *soft* donors [7]. To shed light on this problem, we, thus, decided to prepare and study a mixed complex of the type $[K^IPb^{II}(AcO)_2(SCN)]$, where parts of the ligands were replaced without affecting the main coordination sphere.

Results and Discussion. – Crystals of $[K^IPb^{II}(AcO)_2(SCN)]$ were obtained from 1 equiv. each of $Pb(OAc)_2$ and K^+SCN^- in MeOH by following the so-called 'branch-tube' method (see *Exper. Part*).

The single-crystal X-ray structure of of $[KPb(AcO)_2(SCN)]$ is shown in *Fig. 1,a*, and selected bond distances are collected in the *Table*. The crystals comprise a three-dimensional polymeric network. There are various similarities to polymeric $[Pb(SCN)_2]$[8] and $[Pb(AcO)_2]$ [9], in which adjacent Pb^{2+} and K^+ ions are bridged by acetate and thiocyanate groups. The O-atoms of the AcO^- and the S-atom of the

Table. *Selected Bond Lengths* (Å) *for* $[K^IPb^{II}(AcO)_2(SCN)]$. Symmetry relations are given as footnotes.

Pb Centers		K Centers	
Pb(1)–O(2)	2.44(1)	K(1)–O(6)	2.66(1)
Pb(1)–N(2)[a]	2.56(1)	K (1)–O(10)	2.70(1)
Pb(1)–O(3)	2.57(1)	K (1)–O(4)	2.75(1)
Pb(1)–O(4)	2.68(1)	K (1)–N(1)	2.92(1)
Pb(1)–O(1)	2.72(1)	K (1)–O(8)	3.03(1)
Pb(1)–O(8)	2.73(1)	K (1)–N(3)[a]	3.08(3)
Pb(1)–O(11)	2.97(1)	K (1)–S(2)	3.34(8)
Pb(1)–O(10)	2.98(3)	K (2)–N(3)	2.75(3)
Pb(1)–S(1)[a]	3.26(5)	K (2)–O(3)[b]	2.76(1)
Pb(2)–O(6)	2.40(1)	K (2)–N(2)[a]	2.82(1)
Pb(2)–O(7)	2.46(1)	K (2)–N(3′)	2.84(1)
Pb(2)–O(8)	2.47(1)	K (2)–O(11)[b]	2.92(1)
Pb(2)–O(5)	2.66(1)	K (2)–O(3)	2.96(1)
Pb(2)–O(4)	2.67(1)	K (2)–O(2)	3.07(1)
Pb(2)–O(2)	2.88(1)	K (3)–O(1)[c]	2.74(1)
Pb(2)–O(12)[d]	2.99(1)	K (3)–O(7)[e]	3.75(1)
Pb(2)–S(3′)[f]	3.28(1)	K (3)–O(9)[g]	2.75(1)
Pb(3)–O(9)	2.37(1)	K (3)–N(1)	2.83(2)
Pb(3)–O(12)	2.42(1)	K (3)–O(5)[e]	3.04(1)
Pb(3)–O(11)	2.53(1)	K (3)–O(12)[g]	3.27(2)
Pb(3)–O(5)[h]	2.57(1)	K (3)–S(1)[e]	3.32(7)
Pb(3)–O(10)	2.61(1)		
Pb(3)–S(2)	2.63(7)		
Pb(3)–S(3)[b]	2.58(1)		
Pb(3)–S(3′)[b]	3.64(1)		

[a] $x-1, y, z$. [b] $-x+4, -y+, -z-1$. [c] $x+1, y, z$. [d] $x, y, z+1$. [e] $x-½, -y+½, z-½$. [f] $-x+4, -y+1, z$. [g] $x+½, -y+½, z+½$. [h] $x, y, z-1$.

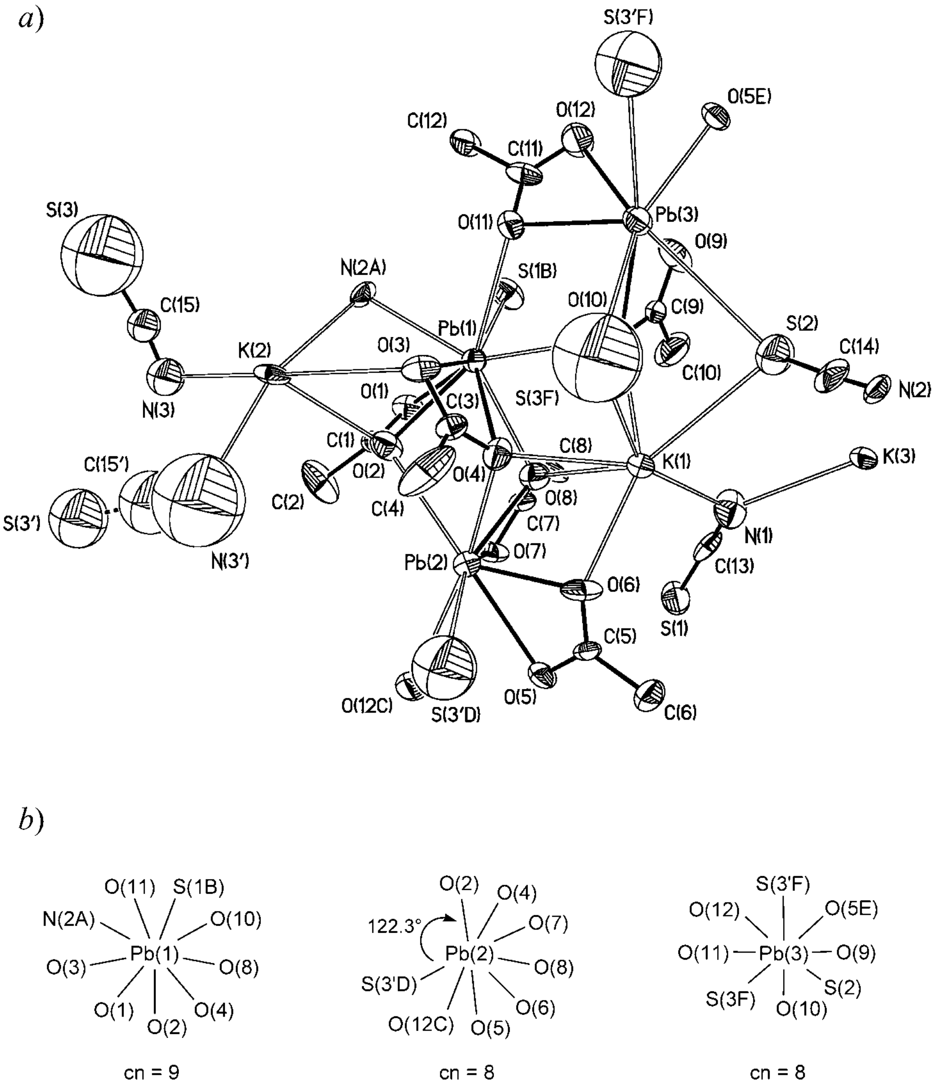

Fig. 1. a) *X-Ray crystal structure* (ORTEP representation) *of* $[\mathrm{K^IPb^{II}(AcO)(SCN)}]_n$. The three thiocyanate (SCN) moieties correspond to S(1)C(13)N(1), S(2)C(14)N(2), and S(3)C(15)N(3). b) *Schematic representation of three different types of* $\mathrm{Pb^{II}}$ *environments* (cn = coordination number). In the vicinity of the eight-coordinated Pb(2) center, there is a hole in the sphere (angle S(3D)–Pb(2)–O(2) of 122.3°).

$\mathrm{NCS^-}$ group(s) are linked to different $\mathrm{Pb^{2+}}$ and $\mathrm{K^+}$ centers. There are three kinds of N-atoms of the $\mathrm{NCS^-}$ anions, linked to different $\mathrm{Pb^{2+}}$ and $\mathrm{K^+}$ ions, and there are also three types of $\mathrm{K^+}$ ions ($\mathrm{KO_4N_2S}$, $\mathrm{KO_4N_3}$, and $\mathrm{KO_5NS}$ partial structures) with coordination numbers of seven. Finally, there are three types of $\mathrm{Pb^{2+}}$ ions: a $\mathrm{Pb(1)O_7NS}$ sphere with a coordination number of nine, and $\mathrm{Pb(2)O_7S}$ and $\mathrm{Pb(3)O_5S_3}$ spheres each with coordination numbers of eight.

In $[\mathrm{KPb(AcO)_2(SCN)}]$, the lone pairs of Pb(1) and Pb(3) are 'inactive' in the solid state. However, the arrangement of O-, N-, and S-atoms suggest a gap or hole in coordination geometry around the $\mathrm{Pb(2)O_7S}$ coordination sphere (*Fig. 1,b*), a gap possibly occupied by a 'stereoactive' electron lone pair. The observed shortening of the Pb–O bond on the side of the $\mathrm{Pb^{2+}}$ ion opposite to the putative lone pair [bond distances for Pb(2)–O(6), Pb(2)–O(2), and Pb(2)–O(12C) of 2.408, 2.888, and 2.992 Å] supports the presence of this feature [10]. Hence, the geometry of the nearest coordination environment of every Pb(2)-atom is likely to be caused by the geometrical constraints of coordinated O-, N-, and S-atoms, and by the influence of a stereochemically 'active' electron lone pair in a hybrid orbital on the metal. Hence, whereas the geometries with respect to Pb(1) and Pb(3) are *holohedral*, that regarding Pb(2) is *hemidirected* (*Fig. 2*).

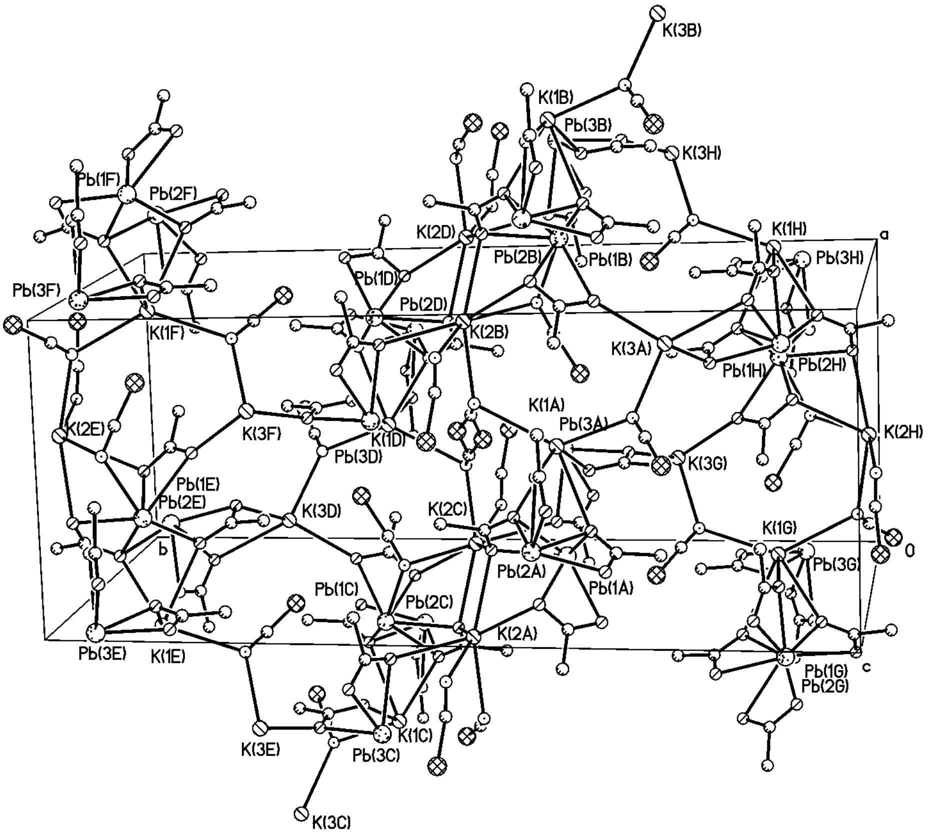

Fig. 2. *Unit cell of* $[\mathrm{K^{I}Pb^{II}(AcO)(SCN)}]_n$. The metal atoms are labeled.

The inactivity of the lone pair in the coordination sphere of Pb(1) is probably due to the nine-fold coordination, in agreement with other nine- and higher-coordinated Pb complexes [6]. The inactive lone pair of Pb(3) and the active one of Pb(2), both with coordination numbers of eight, might be rationalized on the basis of different donor atoms. As shown by *ab initio* calculations [7], the lone pair in complexes with *soft* donor atoms (*e.g.*, S-atoms), are more-likely to be inactive than those with *hard* donors (*e.g.*, O- and N-atoms), as observed in the structures of $[Pb(SCN)_2]$ (holodirected) and $[Pb(AcO)_2]$ (hemidirected). For the Pb(3)-atoms with a PbO_5S_3 coordination sphere, the presence of three donating S-atoms probably renders the lone pair inactive, whereas for Pb(2), with a PbO_7S coordination sphere, the seven hard O-atom donors provoke significant involvement of the 6s orbital in the valence shell and, thus, produce a gap.

The structure of $[K^IPb^{II}(AcO)_2(SCN)]_2$ is interesting because *1*) it respresents a new, rarely observed three-dimensional framework, *2*) it is a new mixed-anion/mixed-metal complex with Pb^{2+} and K^+ ions, and *3*) since this is the first complex with three Pb-atoms in different environments, only one of which having a stereochemically 'inactive' electron lone pair.

Experimental Part

Synthesis of $[K^IPb^{II}(AcO)_2(SCN)]$. A mixture of $Pb(OAc)_2$ (0.36g, 1 mmol) and K^+SCN^- (0.98 g, 1 mmol) was placed in one arm of a branched tube. MeOH was carefully added to fill both arms. Then, the tube was sealed, and the ligand-containing arm was immersed in a bath at 60°, while the other was kept at ambient temperature. After 7 d, white crystals (mp. 132^0) were deposited in the colder arm. They were filtered off, washed with acetone and ether, and dried in air: 0.169 g (40%). IR (selected signals): 658*s*, 1400v*s*, 1520v*s*, 2025v*s*, 2915*w* cm^{-1}. ^1H-NMR ((D_6)DMSO): δ_H 1.7 (*s*). ^{13}C-NMR ((D_6)DMSO): δ_C 27.49; 133.13; 178.81. ^{207}Pb-NMR (DMSO): δ_{Pb} − 723.8. Anal. calc. for $C_5H_6NO_4SKPb$: C 14.18, H 1.41, N 3.30, Pb 49.23; found: C 14.21, H 1.25, N 3.54, Pb 48.52.

X-Ray Crystal Structure. Crystallographic measurements of a single crystal of dimensions $0.25 \times 0.15 \times 0.10$ mm were made at 293(2) K on a *Siemens P3/PC* diffractometer. The intensity data were collected within the range $2.46° \leq \theta \leq 27.06°$, using graphite-monochromated MoK_α radiation (λ 0.71073 Å). Accurate unit-cell parameters and an orientation matrix for data collection were obtained from least-squares refinement. The intensities of 7048 unique reflections were collected, from which 4799 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 the H-atoms were idealized and included in the calculations of the structure factors as fixed contributions. Each H-atom was assigned an isotopic thermal parameter. Crystal data: $C_5H_6KNO_4PbS$, M_r 422.46, monoclinic, space group $P\ 2_1/n$, $a = 10.601(2)$, $b = 26.841(5)$, $c = 11.464(2)$ Å, $\beta = 97.32(3)°$, $V = 3235.6(11)$ Å^3, D_c ($Z = 4$) = 2.602 Mg/m^3, $F(000) = 2304$, $R(wR) =$ 0.0710 (0.1693) for 4799 reflections with $I > 2\sigma(I)$. The full crystallographic data (excluding structure factors) have been deposited with the *Cambridge Crystallography Data Centre* (*CCDC*) as deposition number CCDC-199463. The data can be obtained, free of charge, from the CCDC, 12 Union Road, Cambridge CB21EZ, UK, *via* fax (+44-1223336033) or e-mail (deposit@ccdc.cam.ac.uk).

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