Bachelor Project
University of Zurich

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11/08/2020

Lead Complexes: Crystal Structures Analysis

Lead (Pb) is one of the most abundant toxic metals that causes serious environmental and health problems. Studying the mechanisms of Pb poisoning and its binding preferences can enable designing selective chelating agents to tackle its toxicity.[1] For having an insight into Pb binding characteristic, a total of 130 crystal structures of Pb complexes obtained from the Cambridge Crystallographic Data Centre (CCDC) have been investigated. Most of the crystal structures contain one Pb atom, although some binuclear complexes were also reported (Figure 1).

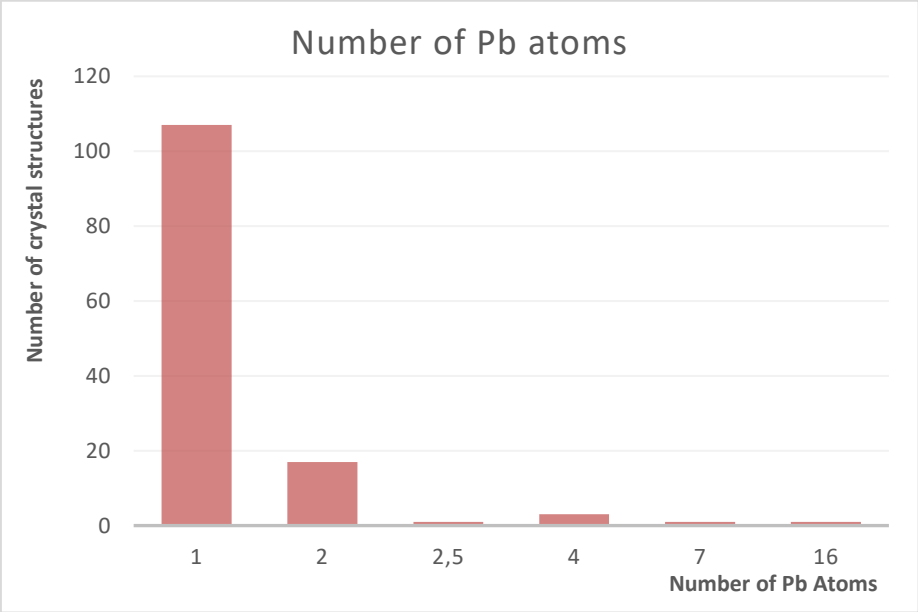


Figure 1. Number of Pb atoms in the crystal structures obtained from CCDC

Ligands

Pb(II) is a borderline metal ion that is known for forming complexes with several functional groups such as COO-, COOH, CONRR', ROR', NRR' and SRR' in small organic molecules as well as in biomolecules (peptides, amino acids, etc.).[2]

The complexes of Pb with various mono or multidentate, open-chain, and macrocyclic ligands were studied. Moreover, its crystal structures with several amino acids such as valine, phenylalanine, glycine, tyrosine, cysteine, arginine, aspartic acid, glutamic acid, isoleucine, or oligosaccharides as cyclodextrin have been analyzed in this study.

Both hard and soft ligands coordinate Pb. In this overview, the hard ligands such as amine, ether, and carboxylate represented the most frequently reported moieties for Pb-coordination. This finding can be explained by the limited numbers of studies conducted using softer ligands to chelate Pb. The abundance of the different coordinating moieties of ligands in the surveyed complexes is shown in Figure 2.

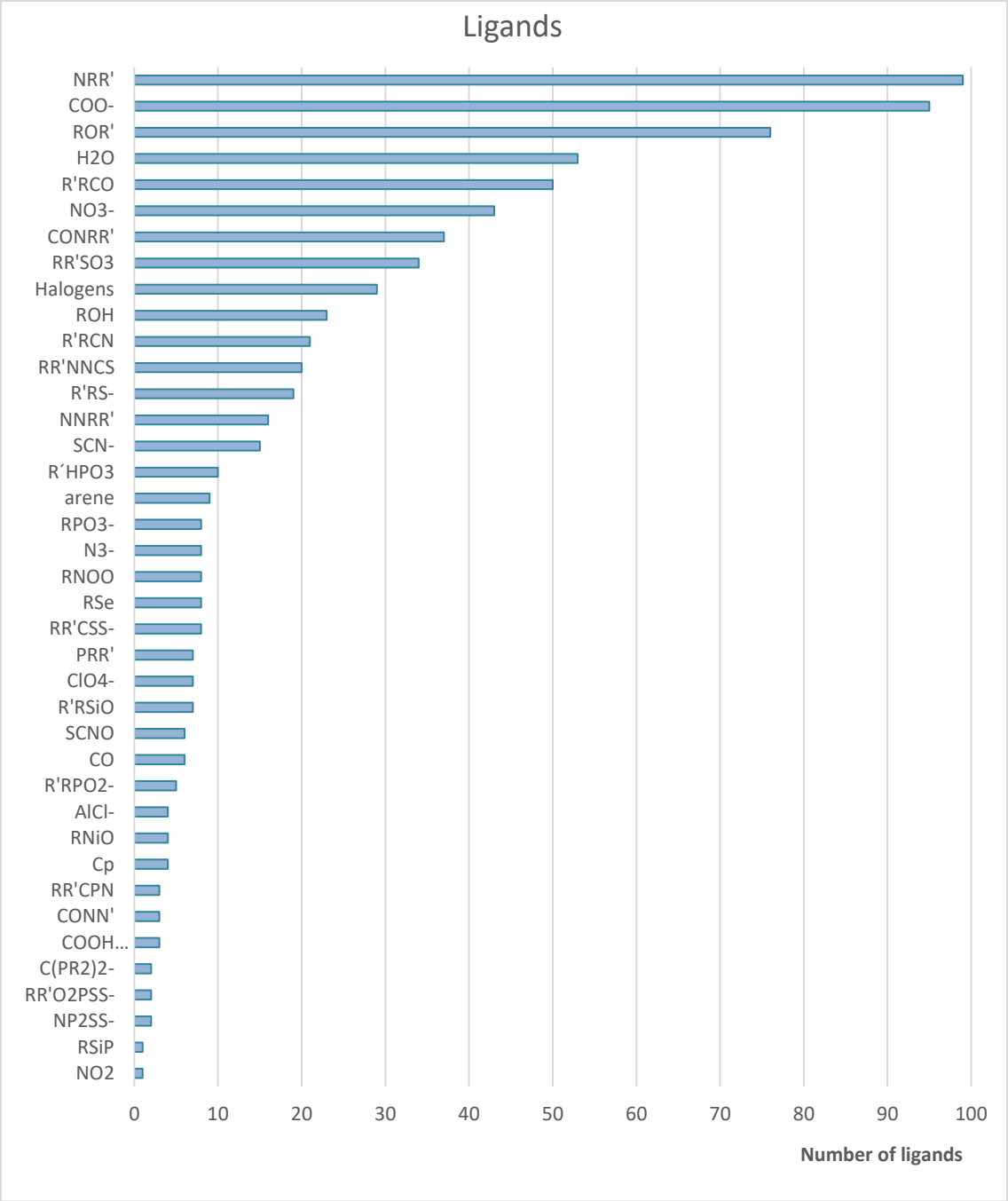


Figure 2. The abundancy of ligands within the studied crystal structures

Some functional groups can bind Pb ions in a multidentate fashion such as a carboxylate moiety. It can act as a monodentate as well as a bidentate ligand by binding Pb to either one or both O atoms. Other possible bidentate moieties are SO_3, NO_3, and $C(PR_2)^{2-}$, which can react with the P binding sites or only *via* the C atom**.** It is worth to mention that the amide group mostly presented as a monodentate ligand coordinating the Pb through the O atom. The ratio of monodentate to bidentate mode of coordination of these functional moieties are described in Figure 3.

Moreover, some ligands showed two possible binding sites, as in the case of the thiocyanate ion $[S{=}C{-}N]^-$, which can bind the metal through the N atom to form isothiocyanate complexes, or through the S atom to form thiocyanate complexes.

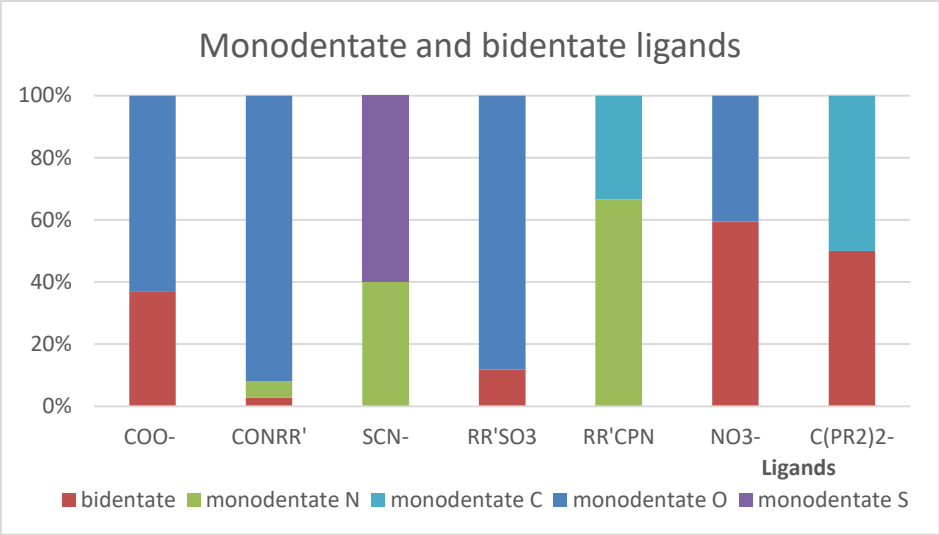


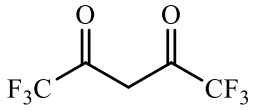
Figure 3. Ratio of monodentate to bidentate coordination for multidentate ligands

Interestingly, some chelators that have two possible binding sites exhibited a preferred site to bind Pb ions (Table 1). This observation is probably due to the difference in the electronegativity and the size of the binding atoms.

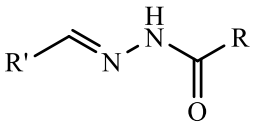
Table 1. Preference between binding sites in ligands. Darker blue indicates bidentate ligands.

	Binding site				
	N	**O**	**P**	**S**	**Halogen**
RR'NNCS-	-	-	-	1	-
RR'O_2PSS-	-	-	-	2	-
NP_2SS-	-	-	-	2	-
Hfa[a]	-	2	-	-	-
Isonicotinohydrazide[b]	1	1	-	-	-

a



b



An appealing example representing this preference is the thiohydroxamato (Figure 4) with various binding sites, including S, N, and O atoms. The O and the S atoms solely complex Pb.[3]

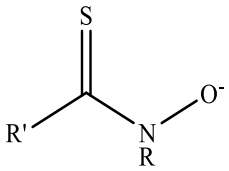


Figure 4. Thiohydroxamato

The following table (Table 2) illustrates the affinity differences between two coordinating moieties in some macrocycle and open-chain ligands.

Comparing the binding sites of ligands, it can be highlighted that the preferable binder for Pb is S atom. However, in presences of different moieties in the same molecule, Pb favoures O atom.

	Between…	Preference	Reference
Macrocycle	O and S	O	[4]
	N and O	O	[5]
	N and Se	N	[6]
	N and F	F	[7]
Open chain	N and S	S	[8]
	N and O	O	[9] [10] [11]
	OH and COOH	COOH	[12]
	N,CO, F and COOH	COOH	[13]

Table 2. Preference between atoms in the same crystal structure

Based on the analyzed data, Pb forms stronger bonds with softer ligands, which are characterized by having a large radius, low oxidation states, high polarization, and low electronegativity. [14,15]

Pb(II) *vs* Pb(IV)

Pb is found predominantly in two oxidative states: Pb(II) and Pb(IV). According to the obtained crystal structures, 97% of them contain Pb(II) cations, and the remaining 3% are bound to Pb(IV) ions. This finding manifested that Pb(II) complexes are more interesting, popular and stable compared to Pb(IV), which are readily reduced.[16]

Coordination Number (CN)

Pb(II) complexes have CNs ranging from 2 to 11, while Pb(IV) complexes have higher CNs - from 6 to 8. Most of the investigated crystal structures possess low CNs, and fewer hold high CNs. The preferred CNs for Pb(II) were found to be 6 and then 4. On the other hand, the most reported CN for Pb(IV) was 7 (Figure 5).

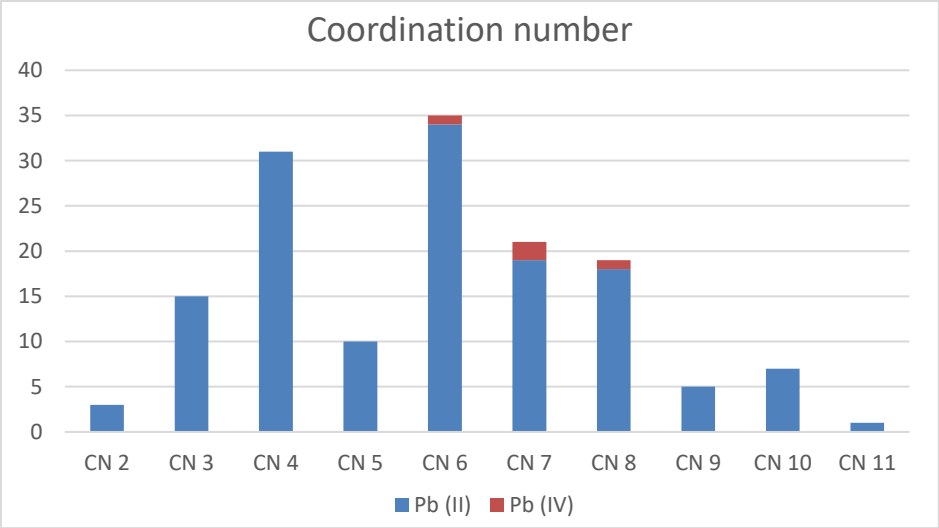


Figure 5. CNs for Pb(II) and Pb(IV)

Holodirected *vs* Hemidirected

Pb(II) ion is being recognized by the presence of the lone pair of electrons in the outer S orbital ($6S^2$). Depending on whether this lone pairs of electrons are stereochemically active or not, the final complex geometry is greatly affected.[2,17]

The complexes geometries are classified into two main structural types: holodirected and hemidirected (Figure 6). Holodirected is the structural geometry in which the bonds with the ligand atoms are distributed throughout the whole space (stereochemically inactive lone pair of electrons). Whereas, in hemidirected geometry, the bonds with the ligand atoms occupied only a part of an encompassing globe (stereochemically active lone pair of electrons).[18]

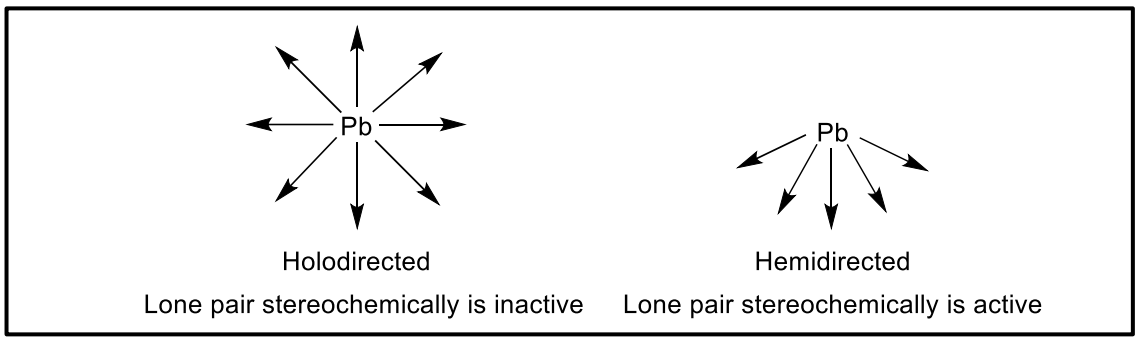


Figure 6. Structural types of the complexes geometries

69.2% of the investigated Pb(II) complexes had a hemidirected configuration, and the lasting 30.8% showed a holodirected arrangement. It can be concluded that the $6S^2$ lone pair is most likely stereochemically active (Figure 7).

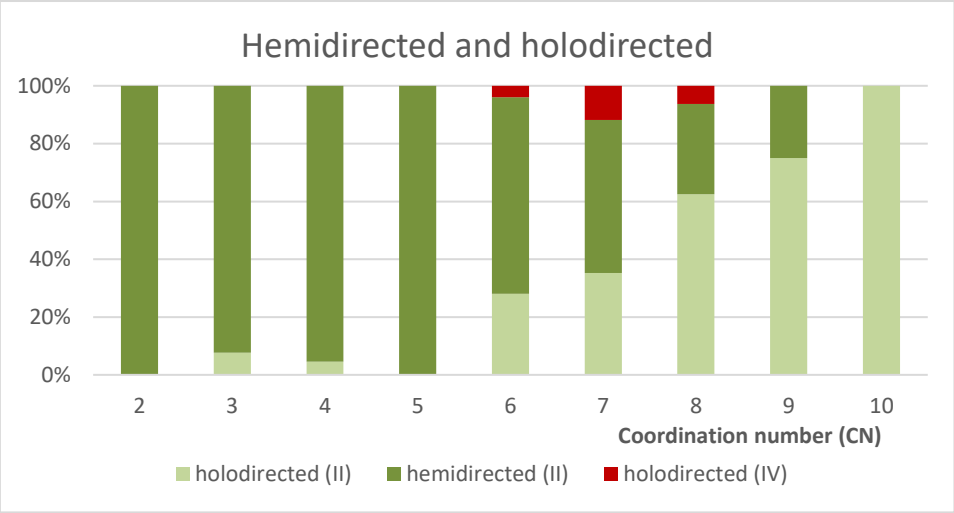


Figure 7. Correlation between Pb(II) and Pb(IV), CNs, and the arrangement of the lone pair. Pb(II) is represented in different tones of green, while Pb(IV) is described in red.

Pb(II) complexes with low CNs (2-5) are arranged in a hemidirected geometry, while the intermediate CNs (6 and 7) display both geometries. Furthermore, a holodirected geometry was reported for the Pb(II) complexes with higher CNs (8-10).

The activity of the lone pair of electrons relayed on two main features of the ligands; the steric strain and the electron-donating ability. Bulky ligands with high CNs lowered the effect of the lone pair of electrons, and eventually lead to the formation of holodirected complex. On the other hand, the electronic effect of the ligands can be examined by comparing the soft and hard ligands. Since soft ligands have a larger size, the charge is delocalized throughout the molecule, and a holodirected configuration is preferred. Whereas, the hard ligands frequently exhibit a hemidirected arrangement (Figure 8).[2]

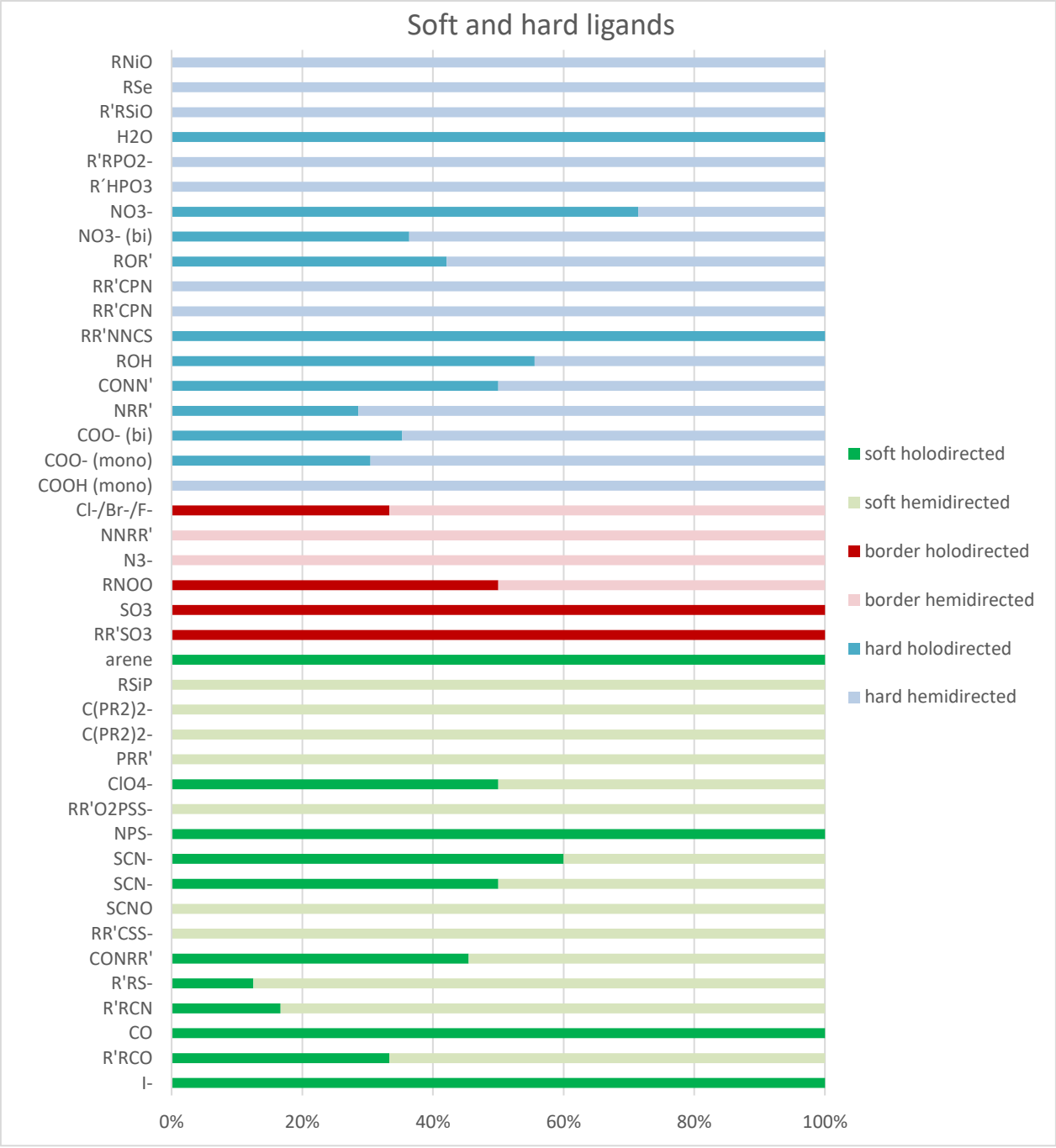
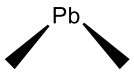


Figure 8. Correlation between soft and hard ligands and hemi/holodirected configurations. Soft ligands are represented in different tones of green, and borderline ligands are represented in red while hard ligands are represented in blue.

Structural Geometry of Complexes

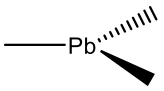
The structural geometry of Pb complexes can be determined by the valence-shell electron-pair repulsion (VSEPR) model.[19] Depending on the stereochemical activity of the lone pair of electrons, the geometries of the complexes can display a distortion (Figure 9).[20]

CN = 2

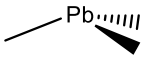


Bent, AX_2E

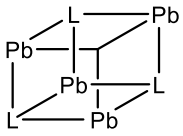
CN = 3



Trigonal planar, AX_3

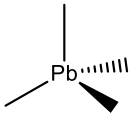


Trigonal pyramidal, AX_3E

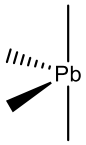


Cubane

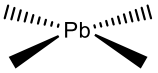
CN = 4



Tetrahedral, AX_4

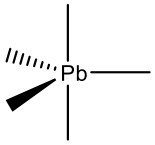


Pseudo trigonal bipyramidal, AX_4

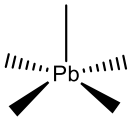


Square planar, AX_4E

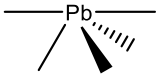
CN = 5



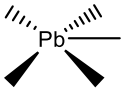
Trigonal bipyramidal, AX_5



Square pyramidal, AX_5



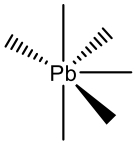
Five coordinated



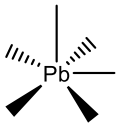
Pentagonal, AX_5E_2

CN = 6

Octahedral, AX_6

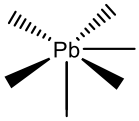


Pseudo pentagonal bipyramidal, AX_6E

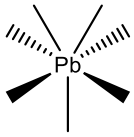


Pseudo pentagonal pyramidal, AX_6E

CN = 7

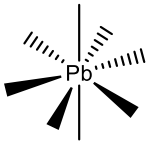


Pentagonal bipyramid, AX_7



Heptacoordinated, AX_7

CN = 8



Hexagonal pyramid, AX_8

Octacoordinated, AX_8

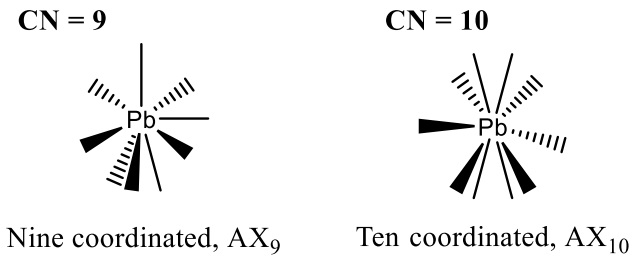


Figure 9. Representation of the possible geometries of Pb complexes

Complexes with a CN = 2 held a bent geometry. While complexes with CN = 3 are arranged mostly in the trigonal pyramidal geometry. In the case of CN = 4 and 5, the lone pairs of electrons are active, and many of the complexes have a distorted square planar, and a square pyramidal configuration, respectively. The preferred arrangements for the structures with a CN = 6 are distorted octahedral and pseudo-pentagonal bipyramidal. Whereas, the crystal structures with higher CNs (7-11) appeared in regular geometries (Figure 10).

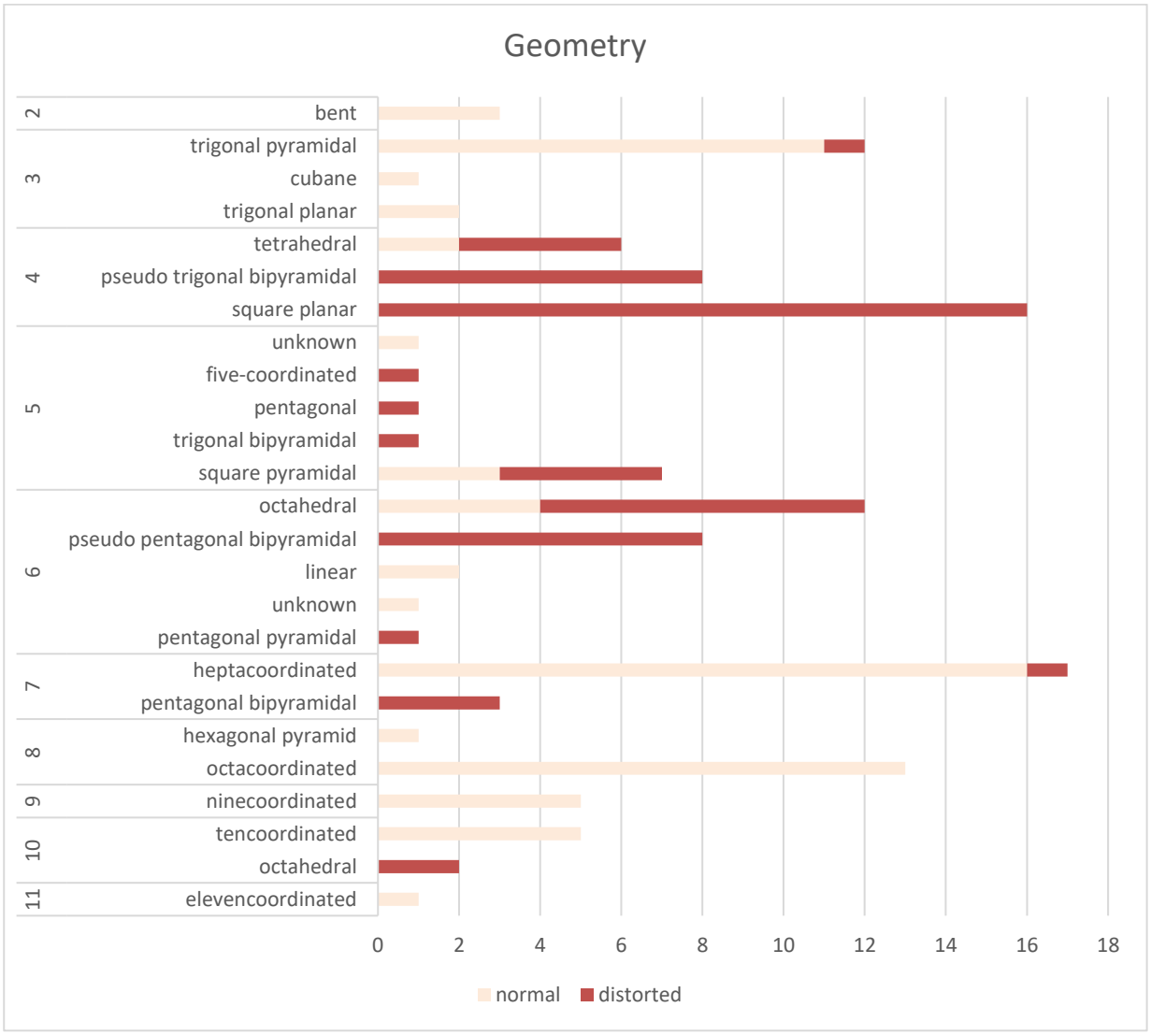


Figure 10. Correlation between the CNs and the geometries of Pb complexes

In some cases, crystal structures for 4 and 6 coordinated complexes have an irregular geometry, which is difficult to be assigned. Moreover, a linear configuration has been assumed in molecules that have Cp (cyclopentadienyl, L_2X) ligands with a CN = 6. Although Cp binds the metal in a penta-hapto (η5-) binding mode, its interaction is typically drawn as a single line.[21]

Conclusion

In this study, 130 crystal structures of Pb complexes have been resolved. According to the collected data, Pb complexes tend to have low CNs, with 6 being the most recorded. The preferred coordinating moieties, within these investigated complexes, are amines, ethers, and carboxylates Interestingly, ligands with various binding sites showed an apparent affinity to bind Pb *via* specific groups.

The lone pair of electrons in the outer S orbital ($6S^2$) of Pb(II) ions affects the geometry of the formed complex. They are stereochemically active in complexes with low CNs, and therefore, a hemidirected configuration was displayed in such complexes. On the contrary, they lose their activity in complexes with higher CNs, and a holodirected arrangement is thus predominant in such crystal structures.

Regarding the complexes' geometry, at CN = 4-6 coordinated molecules displayed distorted geometries. Whereas, crystal structures with CN = 2 and 3 or high CNs (7-11) exhibited regular ones.

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