Lead(II). A Mimic of Copper(II) ... and *vice versa*?

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Mankind knows the metal lead already for thousands of years; e.g., there is a figure in the British Museum made of lead that is by now nearly 6000 years old [1]. Hence, it is not surprising that already Greek and Arab scholars were aware of the toxicity of lead [1]. For example, lead affects the central and nervous systems [2], as well as the genetic and reproductive machinery [1, 3]; indeed, it interferes with the metabolism of other metal ions, like Ca(II), Fe(II/III), Cu(II) or Zn(II) [1, 4]. It is thus surprising that the information available for the interaction of Pb(II) with bio-ligands and the stability of the resulting complexes in aqueous solution is rather scarce. Therefore, estimation procedures are desirable.

The indicated lack of information is probably connected with the ambivalent properties of Pb(II) which originate in its $6s^2$ lone pair [5]. If this lone pair is stereochemically active, it screens one side of Pb(II) and leads to low coordination numbers (CNs) [6, 7]. One distinguishes therefore in a first approximation [8] holodirected (symmetric, with a spherical $6s^2$ lone pair) and hemidirected (distorted, with a non-spherical $6s^2$ lone pair) coordination spheres [7, 9]. For example, S-donor atoms are expected to have a minimal Pb(II) 6s-orbital interaction, leading thus to holodirected structures [10]; such sulfhydryl-Pb(II) complexes can be very stable [4, 11], but this is also true for Pb(II) complexes of negatively charged O sites [4,11]. Indeed, electronegative donor atoms [9], like O sites, favor hemidirected structures [10], whereas "weak" N sites and a high CN favor holodirected arrangements [12].

Evidently Pearson's hard–soft classification fails [4] under these circumstances and this has led Martin to propose his *Stability Ruler* [4, 11] which predicts very similar stabilities for Cu(II) and Pb(II) complexes formed with O-donor sites. One may note that there is a structural similarity between the Jahn-Teller-distorted Cu(II) coordination sphere and the hemidirected one of Pb(II); both like CNs close to four. Indeed, an example for the similarity of the stabilities of complexes formed with O-donor ligands is given in the Table, where

Table. Comparison of the log stability constants of M^{2+} complexes formed with mono- (R-MP^{2-}) and diphosphate (R-DP^{3-}) monoesters (aq. sol.; 25°C; I = 0.1 M, $NaNO_3$)[a)]

L	log $K^{M}_{M(L)}$ for M^{2+} =			
	Cu^{2+}	Zn^{2+}	Cd^{2+}	Pb^{2+}
R-MP^{2-}	2.87 ± 0.06	2.12 ± 0.06	2.44 ± 0.05	2.93 ± 0.08
R-DP^{3-}	5.27 ± 0.04	4.12 ± 0.03	4.27 ± 0.03	5.30 ± 0.15

[a)] Abstracted from Table 6 in [13]. The errors given are three times the standard error of the mean value (σ). R represents in all instances a residue which does not affect metal ion coordination at the phosphate group(s), i.e., neither in a positive nor negative sense.

phosphate monoesters are considered. From the Table it follows that the stabilities of the Cu(II) and Pb(II) complexes are identical within the error limits, whereas the corresponding complexes of Zn(II) and Cd(II) are less stable. There are more such results available which show the analogous pictures [13]. Therefore, one may conclude that Cu(II)-O-donor complexes and their stabilities mimic well the stabilities of the corresponding Pb(II) complexes. Hence, insights into Pb(II) systems for which no experimental data (yet) exist, may thus indirectly be gained. This is of relevance, e.g., for the interaction of Pb(II) with hydroxyl groups [14] and sugar residues [13], where information is obtained in this way.

The affinity of Pb(II) towards N sites is much smaller than towards O sites. In fact, from Martin's *Stability Ruler* it follows [11] that the affinity of ammonia (and imidazole as well) is similar towards Fe(II) and Pb(II) (see also Table 1 in [13]). This helps to rationalize the coordinating properties of Pb(II) towards bio-ligands like adenosine 5'-monophosphate (AMP^{2-}) or guanosine 5'-monophosphate (GMP^{2-}). In Pb(AMP) no macrochelate formation of the phosphate-coordinated Pb(II) with N7 of the purine residue takes place, whereas in Pb(GMP) an interaction with the N7/(C6)O site occurs [13, 15].

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