Supplementary Information

Lead(II) Complex Formation with Glutathione

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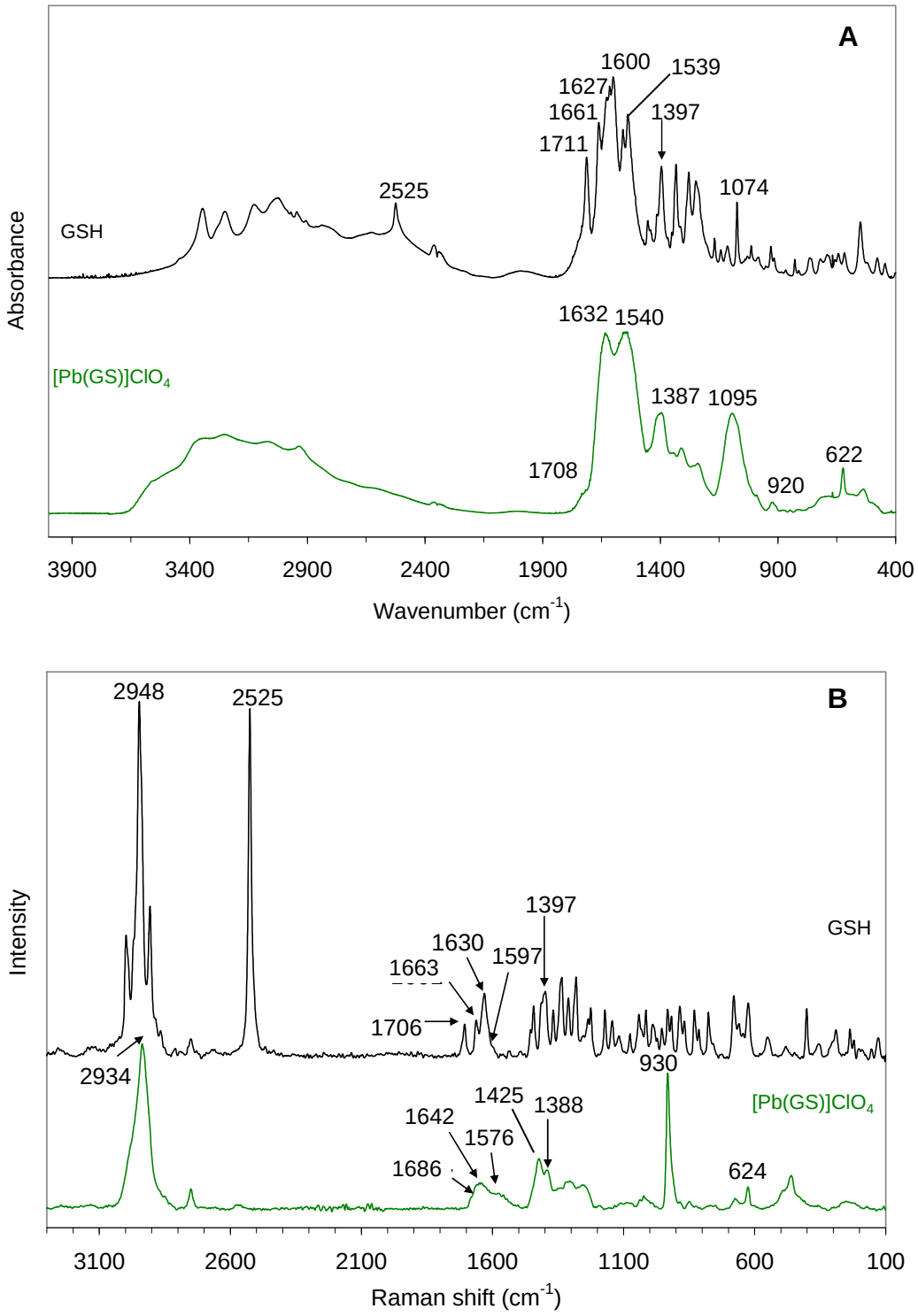


Figure S-1. Baseline corrected (A) IR and (B) Raman spectra for GSH and the $[Pb(AH_2)]ClO_4$ solid.

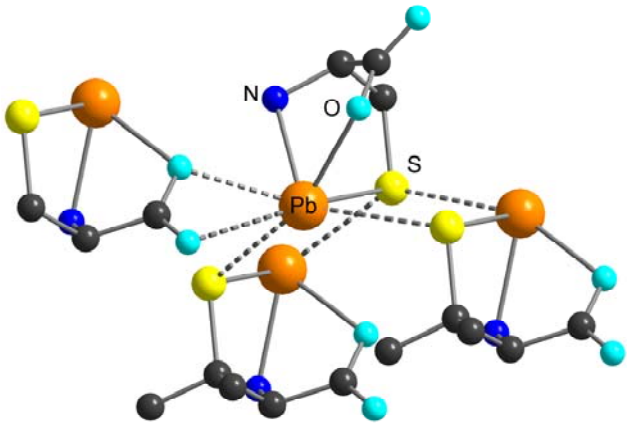


Figure S-2. A fragment of the crystal structure of D-penicillaminato lead(II), PbPen, used to simulate model EXAFS oscillations using FEFF 7.0 program (H atoms were omitted for clarity);[62] the nearest neighbors were found at: Pb-N 2.444(9) Å, Pb-O 2.451(7) Å and Pb-S 2.714(2) Å.

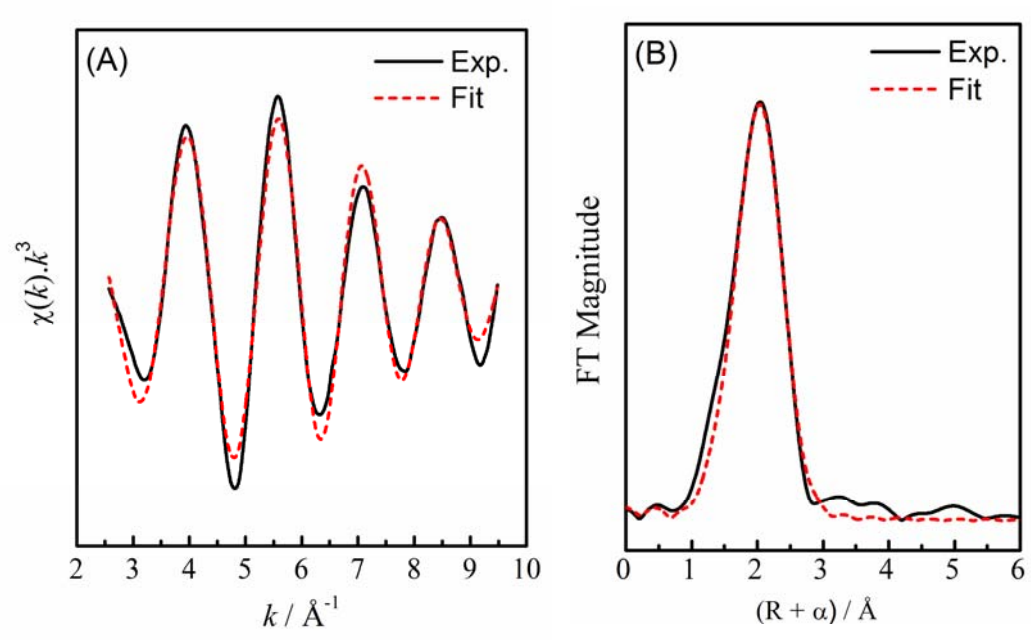


Figure S-3. A) EXAFS curve-fitting for D-penicillaminato lead(II) solid complex (PbPen);
B) corresponding Fourier-transform, with contributions from two Pb-(N/O) 2.42 ± 0.04 Å and one Pb-S 2.68 ± 0.04 Å. Other refined parameters were amplitude reduction factor (S_0^2 = 0.91), ΔE_0 and disorder parameters for Pb-(N/O) and Pb-S paths: σ^2 = 0.0130 ± 0.002 Å^2 and 0.0080 ± 0.002 Å^2, respectively.

Table S-1. Alternative models for EXAFS curve-fitting of the solid compound $[Pb(AH_2)]ClO_4$.[a,b]

Model	Pb-O			Pb-S			Pb-Pb			
	N	*R* (Å)	σ^2 (Å^2)	*N*	*R* (Å)	σ^2 (Å^2)	*N*	*R* (Å)	σ^2 (Å^2)	$\Re$ [c]
1	1.2	2.26	0.0013	1.2	2.63	0.0023				19.5
2	1*f*	2.27	-0.0009	1*f*	2.63	0.0006	1*f*	4.15	0.0052	15.1
3	2*f*	2.28	0.0066	1*f*	2.64	0.0016	2*f*	4.15	0.0106	17.6 *
4	2*f*	2.28	0.0066	1*f*	2.64	0.0016	1*f*	4.15	0.0060	17.3
5	2*f*	2.24	0.0082	2*f*	2.62	0.0079	2*f*	4.14	0.0116	26.5
6	2*f*	2.28	0.0069	1*f*	2.64	0.0019				20.6
				1*f*	3.03	0.0257				

[a] Fitted *k*-range = 2.4 – 9.3 Å^{-1}; $S_0^2 = 0.9$ *f*; *f* = fixed, *N* = coordination number.
[b] Estimated error limit for *R* is ± 0.04 Å and for σ^2 ± 0.002 Å^2.
[c] The residual $\Re$ (%) from the least-squares curve fitting is defined as:

$$\frac{\sum_{i=1}^{N} | y_{exp}(i) - y_{theo}(i) |}{\sum_{i=1}^{N} | y_{exp}(i) |} \text{ X } 100$$

where y_{exp} and y_{theo} are experimental and theoretical data points, respectively.

* The preferred model shown in Figure 1.

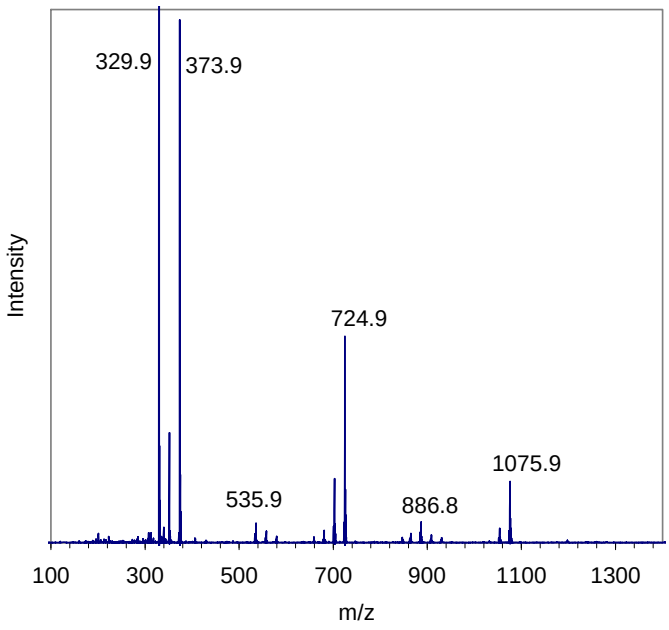


Figure S-4. ESI-MS monitored in the positive ion mode for solution **E** with mole ratio GSH/Pb^{2+} =10.0 (pH 8.5, $C_{Pb^{2+}}$ = 10 mM).

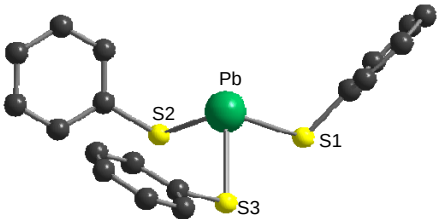
Table S-2. Assignment of Mass Ions in ESI-MS for Solution **E** (GSH/Pb^{2+} = 10.0, pH 8.5, $C_{Pb^{2+}}$ = 10 mM) Measured in the Positive Ion Mode as Shown in Figure S-4.[a]

m/z	Assignment	*m/z*	Assignment
1075.9	$[7Na^+ + (GSH)_3 - 6H^+]^+$	680.9	$[3Na^+ + (GSH)_2 - 2H^+]^+$
930.8	$[5Na^+ + Pb(GSH)_2 - 6H^+]^+$	658.9	$[2Na^+ + (GSH)_2 - H^+]^+$
908.8	$[4Na^+ + Pb(GSH)_2 - 5H^+]^+$	579.8	$[3Na^+ + Pb(GSH) - 4H^+]^+$
886.8	$[3Na^+ + Pb(GSH)_2 - 4H^+]^+$	557.8	$[2Na^+ + Pb(GSH) - 3H^+]^+$
864.8	$[2Na^+ + Pb(GSH)_2 - 3H^+]^+$	535.9	$[Na^+ + Pb(GSH) - 2H^+]^+$
724.9	$[5Na^+ + (GSH)_2 - 4H^+]^+$	373.9	$[3Na^+ + GSH - 2H^+]^+$
702.9	$[4Na^+ + (GSH)_2 - 3H^+]^+$	351.9	$[2Na^+ + GSH - H^+]^+$
		329.9	$[Na^+ + GSH]^+$

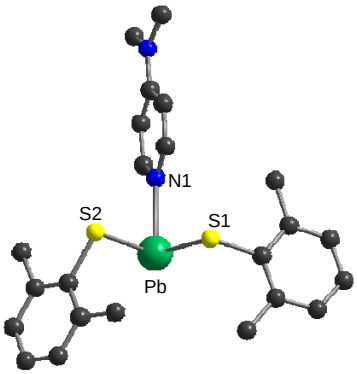
[a] Glutathione, GSH ($C_{10}H_{17}N_3O_6S$) *m* = 307.3

Table S-3. ^{1}H NMR chemical shift changes (Δδ) for GSH resonances after complex formation with Pb^{2+} ions in solutions **A – E** at pH 8.5 ($C_{Pb^{2+}}$ = 10 mM).

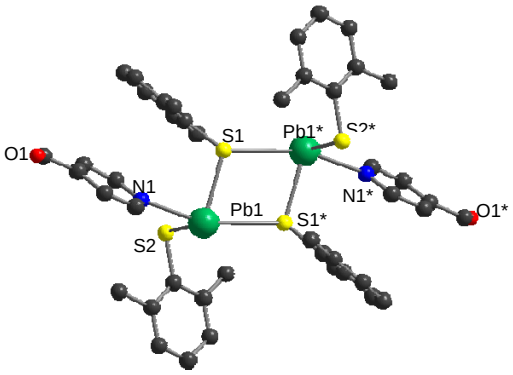
	Δδ (ppm)				
Proton	**A**	**B**	**C**	**D**	**E**
Cys α	0.09	0.01	-0.01	-0.01	-0.01
Cys β_1	0.92	0.65	0.46	0.43	0.22
Cys β_2	0.95	0.69	0.52	0.46	0.22
Glu α	0.03	0.02	0.02	0.02	0.01
Glu β	0.01	0.02	0.01	0.01	0.00
Glu γ	0.00	0.00	0.00	0.00	0.00
Gly α	0.01	0.01	0.00	0.00	0.00



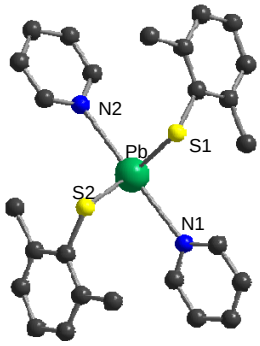
$[Pb(SPh)_3]^-$
PbS_3



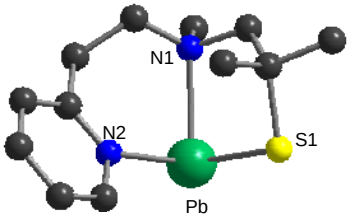
$(2,6\text{-}Me_2C_6H_3S)_2Pb(pyNMe_2)$
PbS_2N



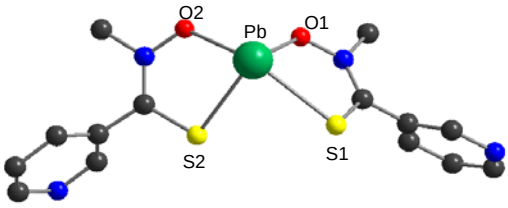
$[(2,6\text{-}Me_2C_6H_3S)_2Pb(pyCOH)]_2$
PbS_2NS'



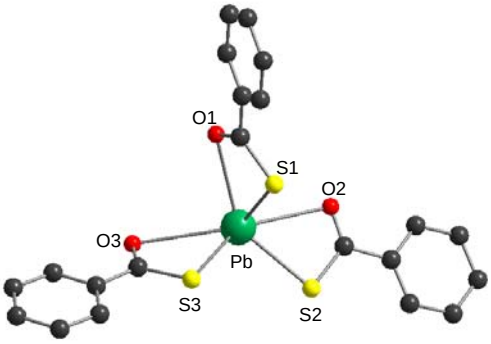
$(2,6\text{-}Me_2C_6H_3S)_2Pb(py)_2$
PbS_2N_2



$[PATH\text{-}Pb]ClO_4$
$PbSN_2$



bis(*N*-methyl-3-pyridothiohydroxamato) lead(II)
PbS_2O_2



$[Pb(SOCPh)_3]^-$
PbS_3O_3

Figure S-5. Structures for Pb^{2+} sulfur-coordinated complexes for which ^{207}Pb NMR chemical shifts and references have been summarized in Table 4; H-atoms were removed for clarity.

Table S-4. Structural parameters derived from EXAFS least-squares curve-fitting for the Pb^{2+}-GSH solutions **C** – **E** (pH 8.5, $C_{Pb^{2+}}$ = 10 mM) at RT using different EXAFS fitting models. [a-c]

Solution	Pb-S			Pb-N			
	N	*R* (Å)	σ^2 (Å^2)	*N*	*R* (Å)	σ^2 (Å^2)	$\Re$
A (Model I)	2.7	2.63	0.0107				28.5
Model II	2 *f*	2.66	0.0122	1 *f*	2.48	0.0036	29.8
Model III	2 *f*	2.65	0.0156	2 *f*	2.51	0.0056	29.4*
B (Model I)	2.9	2.65	0.0070				20.1*
Model II	2 *f*	2.66	0.0053	1 *f*	2.45	0.0067	20.5
Model III	2 *f*	2.66	0.0057	2 *f*	2.49	0.0123	21.2*
C (Model I)	3.3	2.65	0.0068				17.0*
Model II	2 *f*	2.67	0.0040	1 *f*	2.44	0.0019	19.0
Model III	2 *f*	2.67	0.0050	2 *f*	2.48	0.0066	19.1
D (Model I)	3.4	2.65	0.0064				15.9*
Model II	2 *f*	2.68	0.0037	1 *f*	2.46	0.0003	17.6
Model III	2 *f*	2.68	0.0050	2 *f*	2.50	0.0043	17.8
E (Model I)	3.3	2.65	0.0064				16.8*
Model II	2 *f*	2.67	0.0038	1 *f*	2.45	0.0016	19.0
Model III	2 *f*	2.68	0.0048	2 *f*	2.49	0.0059	19.0

[a] Refined *N* accurate within ± 20 %; S_0^2 = 0.9 *f*, *f* = fixed; $\Re$ = residual. [b] Estimated error limits for *R* is ± 0.04 Å and for σ^2 ± 0.002 Å^2; the preferred models labeled with * are shown in Figure 7 and Table 5.

Table S-5. Structural parameters derived from EXAFS least-squares curve-fitting for the Pb^{2+}-GSH frozen glasses (**A*** – **E***) at low temperature using different EXAFS fitting models. [a-c]

Solution	Pb-S			Pb-(N/O)			
	N	*R* (Å)	σ^2 (Å^2)	*N*	*R* (Å)	σ^2 (Å^2)	$\Re$
A* (Model I)	2.9	2.67	0.0077				16.2
Model II	2 *f*	2.68	0.0054	0.8	2.43	0.0076	16.8
Model III	2 *f*	2.68	0.0057	2 *f*	2.50	0.0180	17.9
Model IV	2 *f*	2.67	0.0052	1 *f*	2.40	0.0135	11.4†
	1 *f*	3.18	0.0126				
B* (Model I)	3.4	2.65	0.0048				17.6 †
Model II	2 *f*	2.670	0.0025	1.5	2.46	0.0034	19.9
Model V	3 *f*	2.67	0.0043	1 *f*	2.46	0.0172	17.8
C* (Model I)	3.6	2.65	0.0044				17.2 †
Model V	3 *f*	2.65	0.0034	1 *f*	2.42	0.0082	17.3
D* (Model I)	3.8	2.65	0.0047				17.7 †
Model V	3 *f*	2.66	0.0037	1 *f*	2.45	0.0053	18.4
E* (Model I)	3.5	2.65	0.0038				18.3 †
Model V	3 *f*	2.65	0.0031	1 *f*	2.40	0.0115	18.2

[a] Fitting range: **A*** (2.8 – 11.0 Å^{-1}), **B*** – **E*** (3.0 – 13.8 Å^{-1}); *f* = fixed, $S_0^2 = 0.9f$; $\Re$ = residual; [b] refined *N* accurate within ± 20 %; Estimated error limits: *R* ± 0.04 Å, σ^2 ± 0.001 Å^2; [c] the preferred models labeled with (†) are shown in Table 6, Figures 8 (**A***) and 9 (**B***–**E***).

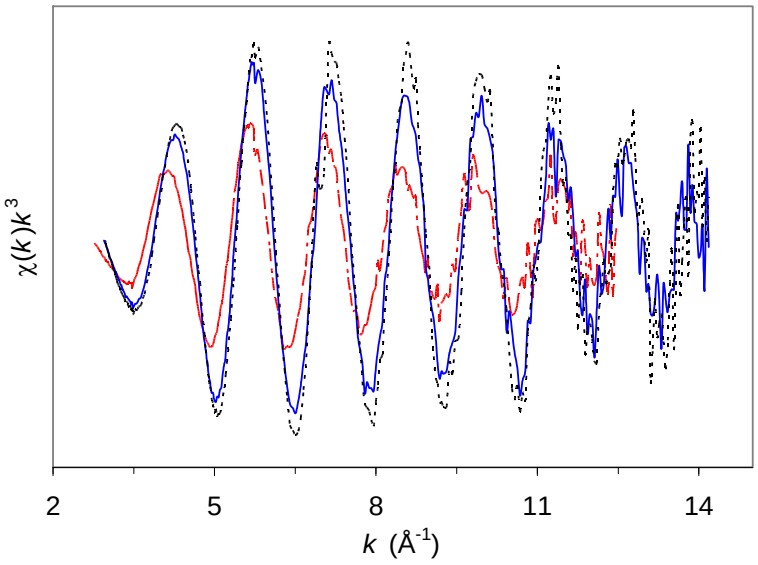


Figure S-6. A comparison of the EXAFS oscillations of 33% v/v glycerol/water frozen glasses with GSH/Pb^{2+} mole ratios 2.0 (**A*** , ·–·–·), 3.0 (**B***, —) and 10.0 (**E***, ·····), $C_{Pb^{2+}}$ = 10 mM, pH 8.5 at LT.

Table S-6. Survey of Pb(II) complexes with PbSN2, PbS2O, PbS2N, PbS2N2, PbS2O2, PbS3N, PbS3 and PbS4) in CSD version 5.32 (Nov 2010)

PbS2N2

	CSD Code	*Pb-S (Å)*	*Pb-N (Å)*
1	BEXLIZ10	2.617	2.591
		2.639	2.691
2	GAGXES	2.608	2.690
		2.608	2.695
3	GAGXIW	2.595	2.652
		2.598	2.814
		2.598	2.653
		2.602	2.668
4	GAGXOC	2.596	2.615
		2.600	2.848
5	HAGSOX	2.617	2.569
		2.653	2.604
6	MILLID	2.838	2.555
		2.920	2.691
		2.922	2.637
		2.922	2.637
		2.905	2.599
		2.905	2.599
7	MILLOJ	2.814	2.533
		2.814	2.533
8	NOGQOQ	2.712	2.401
		2.787	2.469
9	NUFQEL	2.616	2.612
		2.623	2.649
10	PAQVIN	2.673	2.613
		2.713	2.629
11	PAQVOT	2.681	2.575
		2.714	2.604
12	PBMQNL10	2.715	2.481
		2.715	2.481
13	XUSSOT	2.635	2.592
		2.635	2.592
14	XUSSUZ01	2.633	2.550
		2.639	2.626
15	XUVRAH	2.706	2.586
		2.884	2.794
	Pb-X Range	2.595 – 2.922	2.401 – 2.848
	Average	2.707	2.615

PbS2O2

	CSD Code	*Pb-S (Å)*	*Pb-O (Å)*
	ACASIH	2.810	2.361
1		2.810	2.361
2	ACASON	2.675	2.390
		2.675	2.390
3	KEGZAX	2.746	2.383
		2.746	2.383
4	KEGZEB	2.744	2.371
		2.859	2.448
5	WATSEP	2.693	2.408
		2.720	2.418
6	ZOXGAU	2.725	2.349
		2.809	2.497
	Pb-X Range	2.675 – 2.859	2.349 – 2.497
	Average	2.751	2.397

PbS2O

	CSD Code	*Pb-S (Å)*	*Pb-O (Å)*
1	KOYFEJ	2.639	2.496
		2.639	

PbS2N

	CSD Code	*Pb-S (Å)*	*Pb-N (Å)*
1	MPHLPC	2.645	2.606
		2.792	
2	XIRCEH	2.607	2.432
		2.621	
	Pb-X Range	2.607 – 2.792	2.432 – 2.606
	Average	2.666	2.519

PbSN2

	CSD Code	*Pb-S (Å)*	*Pb-N (Å)*
1	HEMSUO	2.599	2.496
			2.528
		2.590	2.494
			2.531
	Pb-X Range	2.590 – 2.599	2.494 – 2.531
	Average	2.595	2.512

PbS3

	CSD Code	*Pb-S (Å)*
1	CAWZIJ	2.553
		2.674
		2.781
2	CUKRUV	2.619
		2.623
		2.647
3	DELFOP	2.633
		2.655
		2.696
4	EBEXEO	2.693
		2.693
		2.693
5	RIPROY	2.683
		2.701
		2.763
6	SEHDOY	2.796
		2.807
		2.856
	Pb-S Range	2.553 – 2.856
	Average	2.698

PbS4

	CSD Code	*Pb-S (Å)*
1	CAWZIJ	2.680
		2.680
		2.896
		2.896
2	LERFUJ	2.650
		2.664
		2.874
		3.292
3	SEHDUE	2.694
		2.706
		2.875
		2.903
	Pb-S Range	2.650 – 3.292
	Average	2.818

PbS3N

	CSD Code	*Pb-S (Å)*	*Pb-N (Å)*
1	XIRBUW	2.626	2.571
		2.664	
		3.174	
2	XIRCAD	2.618	2.497
		2.648	
		3.267	
	Pb-X Range	2.618 – 3.267	2.497 – 2.571
	Average	2.832	2.534

Table S-6a. Survey of PbS2N2 Complexes in CSD version 5.32 (Nov 2010)

CSD Name	Reference	Pb-S (Å)	Pb-N (Å)
BEXLIZ10	L.Ya. Pech, Ya.K. Ozols, S.K. Apinitis, A.P. Sturis *Latv. PSR Zinat. Akad. Vestis, Khim.Ser.* **1982**, 26	2.617 2.639	2.591 2.691
GAGXES	S.E. Appleton, G.G. Briand, A. Decken, A.S. Smith *Dalton Trans.* **2004**, 3515	2.608 2.608	2.690 2.695
GAGXIW	S.E. Appleton, G.G. Briand, A. Decken, A.S. Smith *Dalton Trans.* **2004**, 3515	2.595 2.598 2.598 2.602	2.652 2.814 2.653 2.668
GAGXOC	S.E. Appleton, G.G. Briand, A. Decken, A.S. Smith *Dalton Trans.* **2004**, 3515	2.596 2.600	2.615 2.848
HAGSOX	L. Pech, Yu. Bankovsky, V. Fundamensky, A. Sturis, A. Bruvere *Latv.Khim.Z. (Latv.)(Latvian J.Chem.)* **1992**, 488-4	2.617 2.653	2.569 2.604
MILLID	J.S. Casas, E.E. Castellano, J. Ellena, M.S. Garcia-Tasende, A. Sanchez, J. Sordo, A. Touceda, S.V. Rodriguez *Polyhedron* **2007**,*26*, 4228	2.838 2.920 2.922 2.922 2.905 2.905	2.555 2.691 2.637 2.637 2.599 2.599
MILLOJ	J.S. Casas, E.E. Castellano, J. Ellena, M.S. Garcia-Tasende, A. Sanchez, J. Sordo, A. Touceda, S.V. Rodriguez *Polyhedron* **2007**, *26*, 4228	2.814 2.814	2.533 2.533
NOGQOQ	E. Lopez-Torres, D.G. Calatayud, C.J. Pastor, M.A. Mendiola *Polyhedron* **2008**, *27*, 2507	2.712 2.787	2.401 2.469
NUFQEL	G. Kedarnath, L.B. Kumbhare, S. Dey, A.P. Wadawale, V.K. Jain, G.K. Dey *Polyhedron* **2009**, *28*, 2749	2.616 2.623	2.612 2.649
PAQVIN	M.S. Bharara, C.H. Kim, S. Parkin, D.A. Atwood *Polyhedron* **2005**, *24*, 865	2.673 2.713	2.613 2.629
PAQVOT	M.S. Bharara, C.H. Kim, S. Parkin, D.A. Atwood *Polyhedron* **2005**, *24*, 865	2.681 2.714	2.575 2.604
PBMQNL10	V.M. Agre, E.A. Shugam *Zh.Strukt.Khim.(Russ.)(J.Struct.Chem.)* **1971**,*12*,102	2.715 2.715	2.481 2.481
XUSSOT	H. Fleischer, D. Schollmeyer *Inorg. Chem.* **2004**, *43*, 5529	2.635 2.635	2.592 2.592
XUSSUZ01	H. Fleischer, D. Schollmeyer *Inorg. Chem.* **2004**, *43*, 5529	2.633 2.639	2.550 2.626
XUVRAH	A. Sousa-Pedrares, M.I. Casanova, J.A. Garcia-Vazquez, M.L. Duran, J. Romero, A. Sousa, J. Silver, P.J. Titler *Eur. J. Inorg. Chem.* **2003, 678**	2.706 2.884	2.586 2.794

Table S-6b. Survey of PbS2O2 Complexes in CSD version 5.32 (Nov 2010)

CSD Name	Reference	Pb-S (Å)	Pb-O (Å)
ACASIH	J.A. Lewis, S.M. Cohen *Inorg. Chem.* **2004**, *43*, 6534	2.810 2.810	2.361 2.361
ACASON	J.A. Lewis, S.M. Cohen *Inorg. Chem.* **2004**,*43*, 6534	2.675 2.675	2.390 2.390
KEGZAX	K. Abu-Dari, F.E. Hahn, K.N. Raymond *J. Am. Chem. Soc.* **1990**, *112*, 1519	2.746 2.746	2.383 2.383
KEGZEB	K. Abu-Dari, F.E. Hahn, K.N. Raymond *J. Am. Chem. Soc.* **1990**, *112*, 1519	2.744 2.859	2.371 2.448
WATSEP	K.Abu-Dari, T.B.Karpishin, K.N.Raymond *Inorg.Chem.* , 1993, *32*,3052	2.693 2.720	2.408 2.418
ZOXGAU	S.Rupprecht, S.J.Franklin, K.N.Raymond *Inorg.Chim.Acta* , **1995**, *235*,185	2.725 2.809	2.349 2.497

Table S-6c. Survey of PbS2N and PbS2O Complexes in CSD version 5.32 (Nov 2010)

CSD Name	Reference	Pb-S (Å)	Pb-(N/O) (Å)
MPHLPC	I.G. Dance, P.J. Guerney *Aust. J. Chem.* , **1981**, *34*, 57	2.645 2.792	2.606
XIRCEH	G.G.Briand, A.D.Smith, G.Schatte, A.J.Rossini, R.W.Schurko *Inorg.Chem.* **2007**,*46*, 8625	2.607 2.621	2.432
KOYFEJ	D. Labahn, S. Brooker, G.M. Sheldrick, H.W. Roesky *Z. Anorg. Allg. Chem.* **1992**, *610*, 163	2.639 2.639	2.496

Table S-6d. Survey of PbSN2 Complexes in CSD version 5.32 (Nov 2010)

CSD Name	Reference	Pb-S (Å)	Pb-N (Å)
HEMSUO	R. J. Andersen; R. C. diTargiani; R. D. Hancock; C. L. Stern; D. P. Goldberg; H. A. Godwin, *Inorg. Chem.* **2006,** *45*, 6574.	2.590 2.599	2.494 2.531 2.496 2.528

Table S-6e. Survey of PbS3 Complexes in CSD version 5.32 (Nov 2010)

CSD Name	Reference	Pb-S (Å)
CAWZIJ	P.B. Hitchcock, M.F. Lappert, B.J. Samways, E.L.Weinberg *Chem. Commun.* **1983**,1492	2.553 2.674 2.781
CUKRUV	P.A.W. Dean, J.J. Vittal, N.C. Payne *Inorg.Chem.* **1984**, *23*, 4232	2.619 2.623 2.647
DELFOP	G. Christou, K. Folting, J.C. Huffman *Polyhedron* **1984**, *3*, 1247	2.633 2.655 2.696
DIXKUQ	I.G. Dance, P.J. Guerney, A.D. Rae, M.L. Scudder, A.T. Baker *Aust. J. Chem.* **1986**,*39*, 383 (*Not included in statistics:* three dimers in the unit cell, each with 6 different Pb-S distances)	2.589 2.636 2.726 2.739 2.822 2.854 2.584 2.626 2.633 2.764 2.805 2.911 2.562 2.633 2.780 2.784 2.844 2.919
EBEXEO	B.M. Bridgewater, G. Parkin *J. Am. Chem. Soc.* **2000**, *122*, 7140	2.693 2.693 2.693
RIPROY	Zhi-Gang Ren, Xiao-Yan Tang, Li Li, Guang-Fei Liu, Hong-Xi Li, Yang Chen, Yong Zhang, Jian-Ping Lang *Inorg. Chem. Commun.* **2007**, *10*, 1253	2.683 2.701 2.763
SEHDOY	H.-U. Hummel, H. Meske *Z. Naturforsch., B:Chem. Sci.* **1989**,*44*,1531	2.796 2.807 2.856

Table S-6f. Survey of PbS3N Complexes in CSD version 5.32 (Nov 2010)

CSD Name	Reference	Pb-S (Å)	Pb-N (Å)
XIRBUW	G.G. Briand, A.D. Smith, G. Schatte, A.J. Rossini, R.W. Schurko *Inorg. Chem.* **2007**, *46*, 8625	2.626 2.664 3.174	2.571
XIRCAD	G.G. Briand, A.D. Smith, G. Schatte, A.J. Rossini, R.W. Schurko *Inorg. Chem.* **2007**, *46*, 8625	2.618 2.648 3.267	2.497

Table S-6g. Survey of PbS4 Complexes in CSD version 5.32 (Nov 2010)

CSD Name	Reference	Pb-S (Å)
CAWZIJ	P.B. Hitchcock, M.F. Lappert, B.J. Samways, E.L. Weinberg *Chem. Commun.* **1983**,1492	2.680 2.680 2.896 2.896
LERFUJ	B. Krebs, A. Brommelhaus, B. Kersting, M. Nienhaus *Eur. J. Solid State Inorg. Chem.* **1992**, *29*, 167	2.650 2.664 2.874 3.292
SEHDUE	H.-U. Hummel, H. Meske *Z. Naturforsch., B: Chem. Sci.* **1989**, *44*,1531	2.694 2.706 2.875 2.903