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Supporting information for article:

Ψ-Polyhedral symbols for coordination geometries of lead(II) with stereochemically active lone pair

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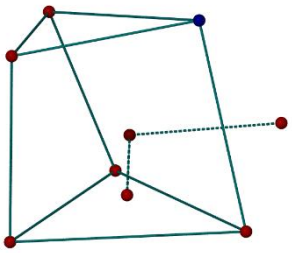
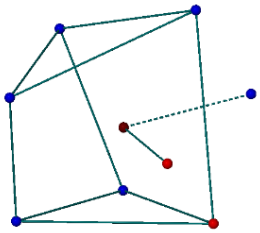
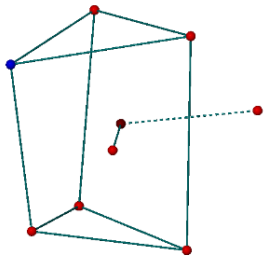
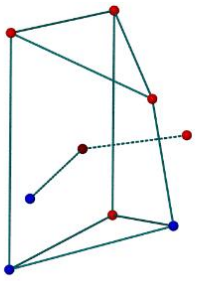
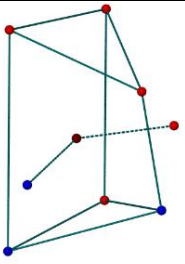
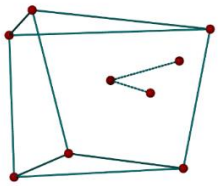
Table S1. CH&N % recalculated from published (*Yin et al.*, 2019) crystal structures

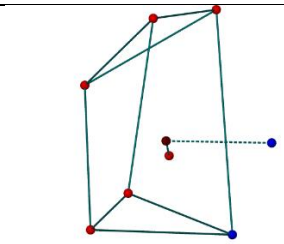
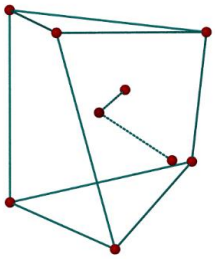
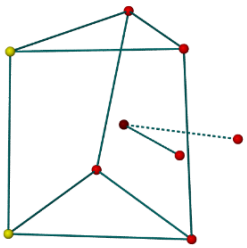
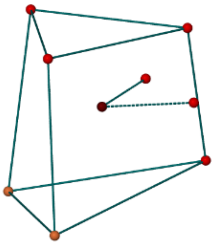
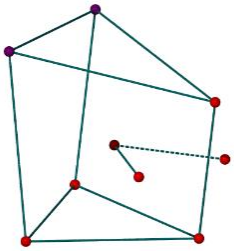
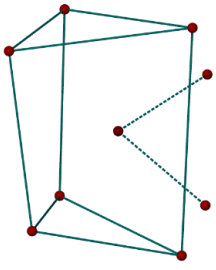
Compound	**Formula**	**CH&N % (calculated)**	**CH&N % (found)**
$[Pb_2(H_2O)_{0.5}(C_4H_9NO)_{0.5}(C_{13}H_7NO_4)_2]\cdot 1.5(C_4H_9NO)$	$C_{34}H_{33}N_4O_{10.5}Pb_2$	C 37.81 H 3.08 N 5.19	C 38.42 H 2.77 N 5.18
$[Pb_2(H_2O)_{0.5}(C_3H_7NO)_{0.5}(C_{13}H_7NO_4)_2]\cdot 1.5(C_3H_7NO)$	$C_{32}H_{29}N_4O_{10.5}Pb_2$	C 36.53 H 2.78 N 5.37	C 36.88 H 3.20 N 5.83
$[Pb_2(H_2O)_{0.25}(C_3H_7NO)_{0.75}(C_{13}H_7NO_4)_2]\cdot C_6H_{15}N\cdot 0.5(C_3H_7NO)$	$C_{36}H_{38.5}N_{4.25}O_{9.5}Pb_2$	C 39.42 H 3.51 N 5.43	C 39.92 H 3.45 N 5.11

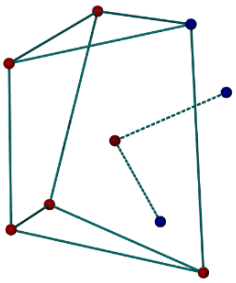
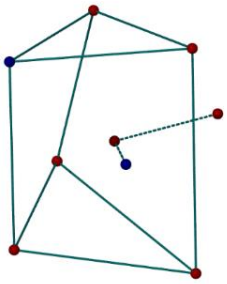
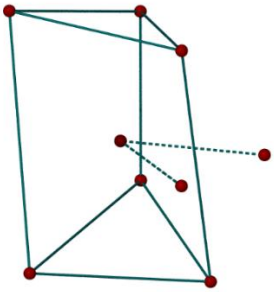
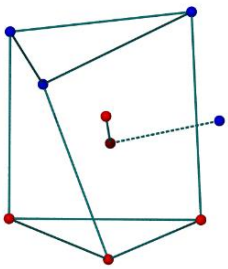
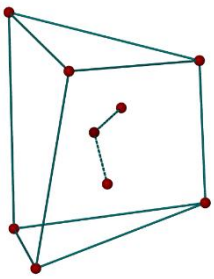
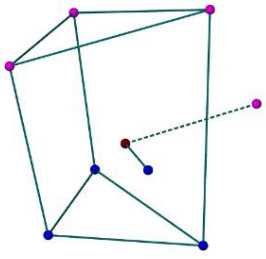
Table S2. Refinements and electron count in voids (voids on a center-of-symmetry) from published (Yin *et al.*, 2019) diffraction data

Structure	**1**	**2**	**3**
R	0.028	0.035	0.026
S	1.013	1.078	1.021
w	$[\sigma^2 + (0.035P)^2 + 0.774P]^{-1}$	$[\sigma^2 + (0.057P)^2 + 1.846P]^{-1}$	$[\sigma^2 + (0.031P)^2]^{-1}$
No. electrons	155	96	99
Volume of void, Å^3	534	526	485
Recovered electrons in void/unit cell	155	96	99
Solvent molecules squeezed/ unit cell	3 DMA	3 DMF	2 NEt_3 + 1DMF
Number of electrons squeezed	144	120	156
Old CCDC Number	1943141	1943138	1943143
New CCDC Number	2069799	2069800	2069801

Table S3. Lead(II) coordination assigned as Ψ–tricapped trigonal prism

Pb(II) compound		**IUCr/IUPAC**	**Ref.**
$[Pb_2(H_2O)_{0.25}(C_3H_7NO)_{0.75}(C_{13}H_7NO_4)_2]\cdot 1.5(C_3H_7NO)$ Pb at (0.5087, 0.8373, 0.0453)		Ψ-TRPS-9	This work
$Pb_2(NO_3)_2(C_2N_3)_2(C_{16}H_{10}N_4O_2)_4$		Ψ-TRPS-9	Marandi *et al.*, 2019
$Pb(C_7H_3NO_4)$		Ψ-TRPS-9	Lush & Shen, 2011
$Pb_4(C_{12}H_8N_2)_2(C_9H_6NO)_4(C_5H_2ClO_2S)_4$ Pb at (0.5240,0.3350,0.2262)		Ψ-TRPS-9	Jennifer & Muthiah, 2014
$Pb(ClO_4)(C_{12}H_8N_2)(C_2H_3O_2)$		Ψ-TRPS-9	Hall *et al.*, 2000
$Pb_4(H_2O)(C_7H_{12}NO_5P)(C_8H_3O_5S)_2]\cdot 2H_2O$ Pb at (0.8524, 0.7954, 0.3525)		Ψ-TRPS-9	Chen *et al.*, 2011
$Pb(C_{10}H_8N_2)(C_7H_4O_6S)\cdot 0.5(C_{10}H_8N_2)$		Ψ-TRPS-9	Fan & Zhu, 2007

			
$Pb2(C_3H_7NO)(C_9H_3O_6)_2$		Ψ-TRPS-9	Gao *et al.*, 2019
$2(C_3H_{10}N)\cdot Pb_4Cl_2(C_{12}H_6O_4)_4$		Ψ-TRPS-9	Lin *et al.*, 2020
$2(C_2H_8N)\cdot Pb_4Br_2(C_{12}H_6O_4)_4$		Ψ-TRPS-9	
$2(C_2H_8N)\cdot Pb_4I_2(C_{12}H_6O_4)_4$			
$PbCu_2(NO_3)_2(C_{10}H_{20}N_2O_2)$		Ψ-TRPS-9	Chakraborty & Mohanta, 2017

$Pb(H_2O)_3(C_{18}H_{14}N_8O_4)\cdot H_2O$		Ψ-TRPS-9	Li *et al.*, 2021
$Pb(C_9H_7N_4O_2)(C_2H_3O_2)$		Ψ-TRPS-9	
$Pb(C_{10}H_{14}O_4)$ Pb at (0.7934, 0.2692, 0.7062)		Ψ-TRPS	Zhu *et al.*, 2016
$Pb(C_{24}H_{16}N_2)_2(C_{10}H_6F_3O_2)_2$		Ψ-TRPS-9	Hosseini *et al.*, 2013
$Pb(NO_3)(C_6H_4NO_3)$		Ψ-TRPS-9	Jin, 2020
$Pb(SCN)_2(C_4H_6N_2)$		Ψ-TRPS-9	Mohammadi *et al.*, 2019

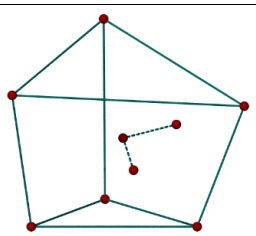
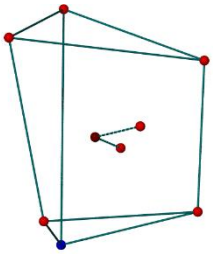
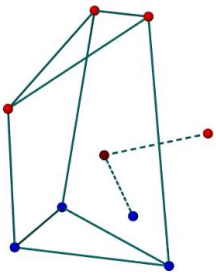
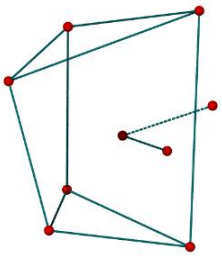
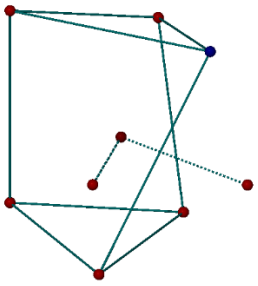
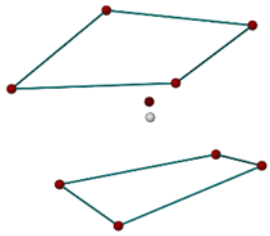
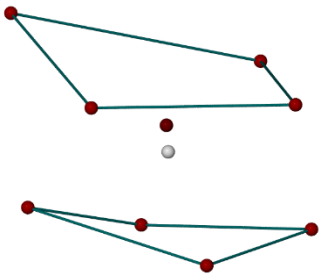
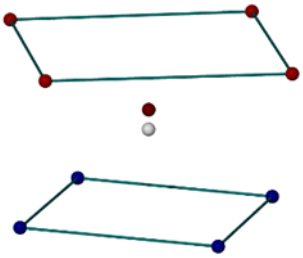
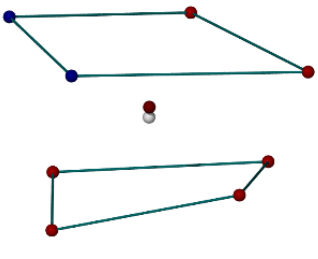
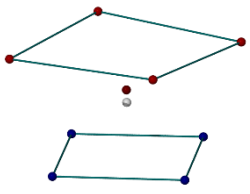
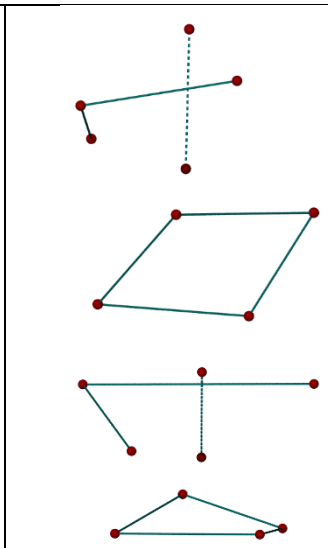
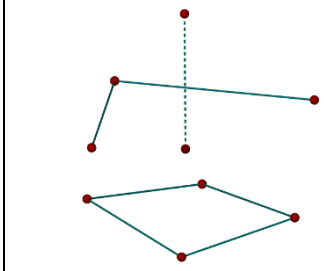
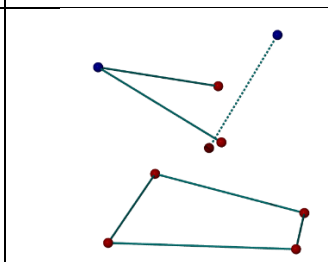
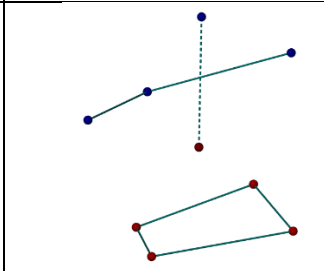
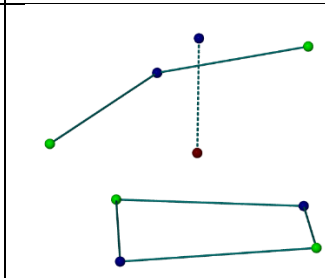
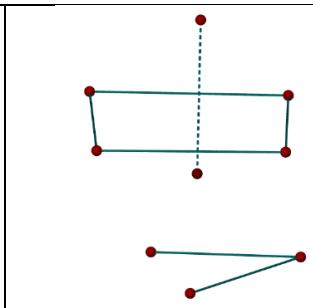
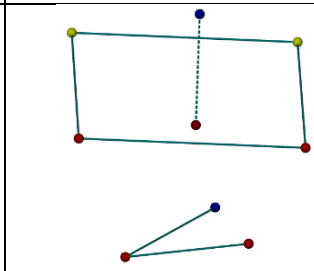
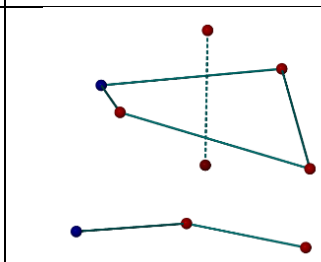
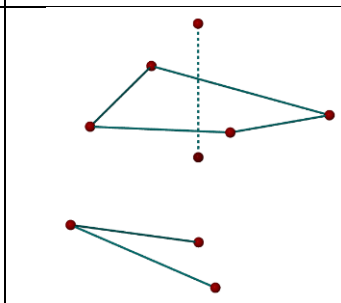
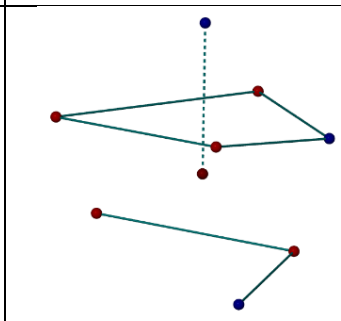
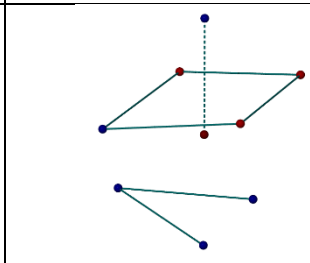
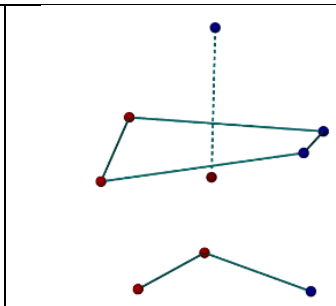
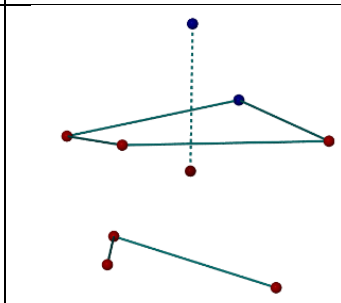
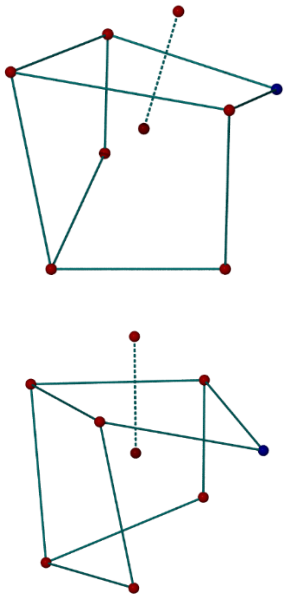
$Pb_4(H_2O)(C_5H_4NO_2)_8$ Pb at (0.5133, 0.8733, 0.9954)		Ψ-TRPS-9	Kowalik *et al.*, 2017
$Pb(H_2O)_2(C_7H_3NO_4)(C_7H_4NO_4)\cdot H_2O$		Ψ-TRPS-9	Harrowfield *et al.*, 2003
$Pb(H_2O)(C_{12}H_8N_2)_2(C_6H_6NO_3S)_2$		Ψ-TRPS-9	Cheng *et al.*, 2014
$Pb_2(C_9H_3O_6)(C_9H_4O_6)\cdot 2H_2O$ Pb at (0.4259,0.7468,0.8557)		Ψ-TRPS-9	Hayati *et al.*, 2018
$Pb(H_2O)(C_6H_4NO_2)_2$		Ψ-TRPS-9	Zhou *et al.*, 2007

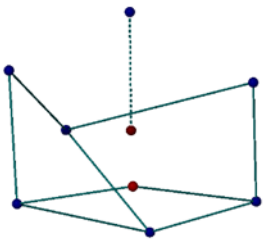
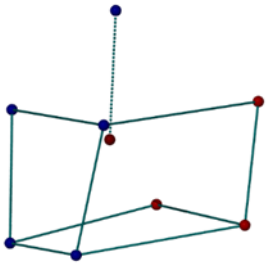
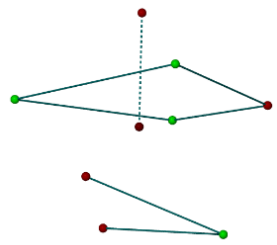
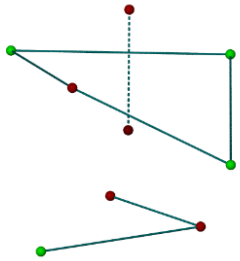
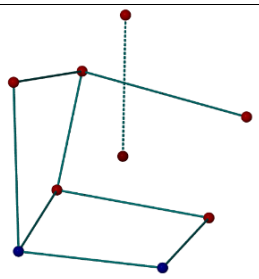
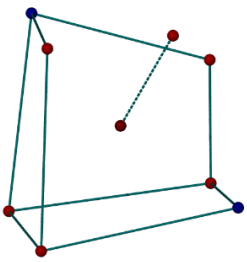
Table S4. Lead(II) coordination assigned as Ψ–monocapped square antiprism, Ψ–monocapped cube and Ψ–bicapped cube

Pb(II) compound		**IUCr/IUPAC**	**Ref.**
$Pb_3(C_7H_{12}NO_6P)_2(C_7H_4O_6S)].2H_2O$ Pb at (1.2416, 0.0878, 0.4927)	 Pb–centroid 0.37 Å	Ψ-SAPRS-9	Chen *et al.*, 2011
$Pb(C_{10}H_{14}O_4)$ Pb at (0.9417, 0.7655, 0.6773)	 Pb–centroid 0.40 Å	Ψ-SAPRS-9	Zhu *et al.*, 2016
$Pb(NO_3)_2(C_{16}H_{32}N_8O_4)\cdot 3.5H_2O$	 Pb–centroid 0.30 Å	Ψ-SAPRS-9	Cuenot *et al.*, 2008
$PbC_{20}H_{14}N_4O_2)(C_8H_4O_4)$	 Pb–centroid 0.22 Å	Ψ-SAPRS-9	Yan *et al.*, 2013
$Pb(C_{16}H_{32}N_8O_4)(CF_3O_3S)_2$	 Pb–centroid 0.29 Å	Ψ-SAPRS-9	Lyczko *et al.*, 2020

$Pb_4(H_2O)(C_7H_{12}NO_5P)(C_8H_3O_5S)_2]\cdot 2H_2O$ Pb at (1.0282, -0.2667, -0.0103) $Pb_3(C_7H_{12}NO_6P)_2(C_7H_4O_6S)].2H_2O$ Pb at (0.8665, 0.0909, 0.3887)		Ψ-SAPRS-9 Ψ-SAPRS-9	Chen *et al.*, 2011
$Pb(C_4H_4O_6)$		Ψ-SAPRS-9	Weil, 2014
$Pb(C_6H_4NO_2)_2$		Ψ-SAPRS-9	Shahverdizadeh *et al.*, 2008
$Pb(NO_2)_2(C_{12}H_8N_2)_2$		Ψ-SAPRS-9	Morsali, 2005
$Pb(C_4H_3N_2S)_2$		Ψ-SAPRS	Schwade *et al.*, 2015

$Pb_2(W_{12}SiO_{36})(C_3H_7NO)_{16}$		*ψ*-SAPRS-9	Pang *et al.*, 2019
$PbI(C_9H_7N_4O_2)$		*Ψ*-SAPRS-9	Li *et al.*, 2021
$Pb(H_2O)(NO_3)_2(C_{12}H_8N_2)$		*Ψ*-SAPRS	Zhang & Lu, 2005
$Pb_2(H_2O)(C_{10}H_8N_2)(C_8H_3F_2O_4)\cdot 3H_2O$ Pb at (0.1766, 0.5038, -0.0816)		*Ψ*-SAPRS-9	Song *et al.*, 2014
$Pb(NO_3)(C_5H_6N_2O)_3]_2\cdot 2NO_3$		*Ψ*-SAPRS-9	Masternak *et al.*, 2005
$Pb(H_2O)_2[B(CN)_4]_2$		*Ψ*-SAPRS-9	Siegesmund *et al.*, 2021

$Pb[B(CN)_4](C_2H_3O_2)\cdot C_2H_6O$		Ψ-SAPRS-9	
$Pb2(C_{12}H_8N_2)_2(C_7H_4C1O_3)_4\cdot 2H_2O$		Ψ-SAPRS-9	Tang & Wen, 2021
$[Pb_2(H_2O)_{0.5}(C_4H_9NO)_{0.5}(C_{13}H_7NO_4)_2]\cdot 1.5(C_4H_9NO)$ Pb at (0.4855, 0.4368, 0.1638) $Pb_2(H_2O)_{0.5}(C_3H_7NO)_{0.5}(C_{13}H_7NO_4)_2]\cdot 1.5(C_3H_7NO)$ Pb at (0.4870, 0.9424, 0.664)		Ψ-CUS-9 Ψ-CUS-9	This work

$Pb_2(C_{51}H_{47}N_{15}O_2)(CH_4O)(CF_3O_3S)]\cdot 3CF_3O_3S\cdot 2CH_4O\cdot 2H_2O$ Pb at (0.1421, 0.3699, 0.6108)		Ψ-CUS-9	Lobo *et al.*, 2019
$[Pb_2(C_{51}H_{47}N_{15}O_2)(CH_4O)(CF_3O_3S)]\cdot 3CF_3O_3S\cdot 2CH_4O\cdot 2H_2O$ Pb at (0.7551, 0.3882, 0.9049)		Ψ-CUS-9	
$Pb(NO_3)_2(C_7H_6N_2S)_2$		Ψ-CUS-9	Fan & Zhu, 2006
$Pb(NO_3)_2(C_3H_5N_3S)_4$		Ψ-CUS-9	
$[Pb_3(C_{12}H_8N_2)_3(C_7H_3O_6S)_2$ Pb at (0.8519, 0.3547, 0.2850)		Ψ-CUS-9	Imran *et al.*, 2015
$Pb(C_6H_4NO_2)_2$		Ψ-CUS-9	Etaiw *et al.*, 2018

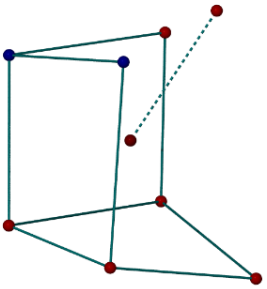
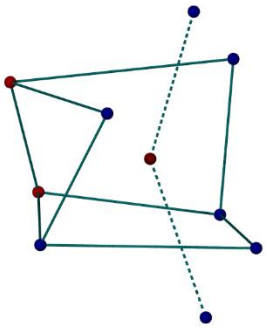
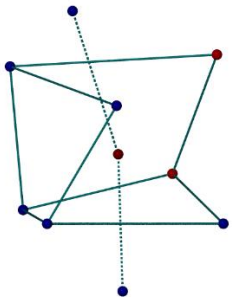
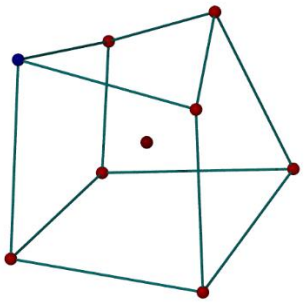
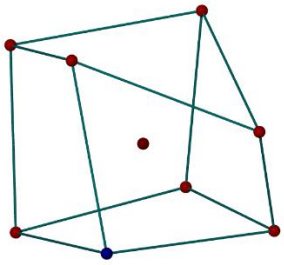
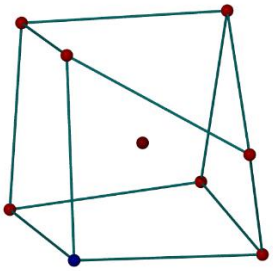
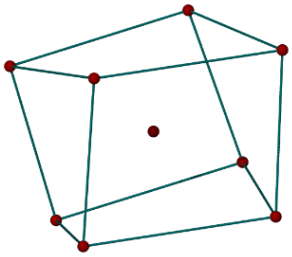
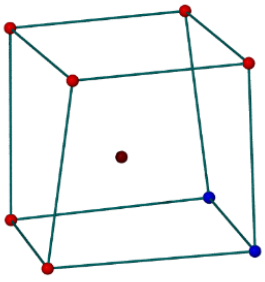
$Pb(NO_3)_2(C_{14}H_{12}N_2)$		*Ψ*-CUS-9	Morsali, 2004
$[Pb_2(C_{51}H_{47}N_{15}O_2)(CF_3O_3S)_2]\cdot 3CF_3O_3S\cdot C_2H_3N$ Pb at (0.6666, 0.2320, 1.0034)		*Ψ*-CUS-10	Lobo *et al.*, 2019
$[Pb_2(C_{51}H_{47}N_{15}O_2)(CF_3O_3S)_2]\cdot 3CF_3O_3S\cdot C_2H_3N$ Pb at (0.7551, 0.3882, 0.9049)		*Ψ*-CUS-10	

Table S5. Lead(II) coordination assigned as 8-vertex polyhedral (stereochemically-inert lone pair)

Pb(II) compound		**IUCr/IUPAC**	**Ref.**
$[Pb_2(H_2O)_{0.5}(C_4H_9NO)_{0.5}(C_{13}H_7NO_4)_2]\cdot 1.5(C_4H_9NO)$ Pb at (-0.1472, -0.4080, 0.0488)		CU-8	This work
$[Pb_2(H_2O)_{0.5}(C_3H_7NO)_{0.5}(C_{13}H_7NO_4)_2]\cdot 1.5(C_3H_7NO)$ Pb at (-0.1460, 0.0933, 0.5471)		CU-8	
$Pb_2(H_2O)_{0.25}(C_3H_7NO)_{0.75}(C_{13}H_7NO_4)_2]\cdot 1.5(C_3H_7NO)$ Pb at (1.1443, 0.9460, 0.9024)		CU-8	
$Pb_5O(C_{12}H_6O_4)_4$ Pb at (0, 1.1331, ¼)		CU-8	Zhou, 2020
$Pb_2(C_{14}H_{12}N_2)_2(C_{11}H_8F_3O_3)_4$		CU-8	Marandi & Krautscheid, 2009

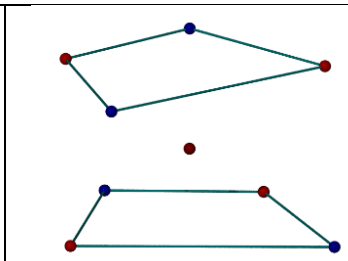
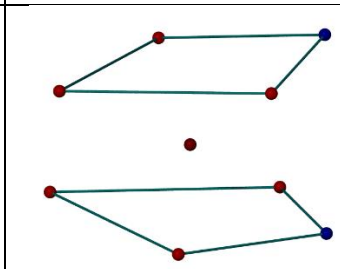
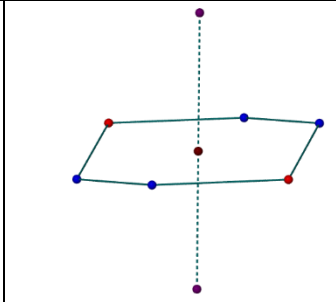
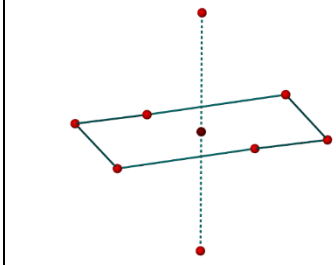
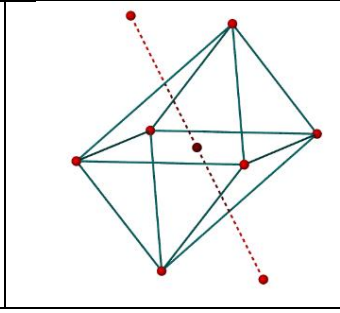
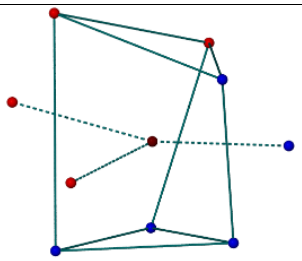
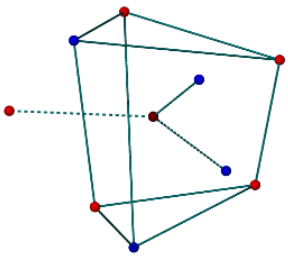
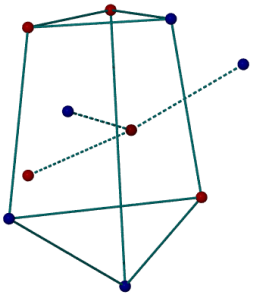
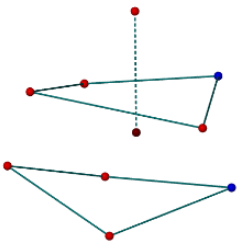
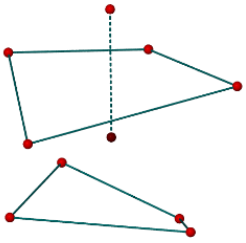
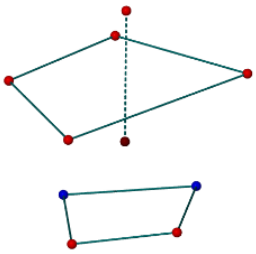
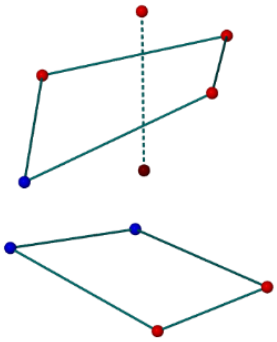
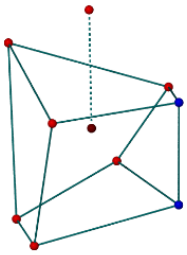
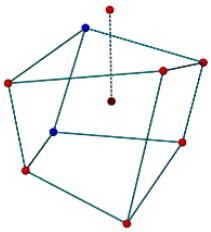
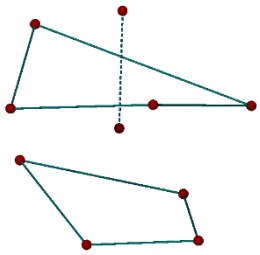
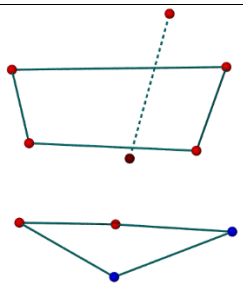
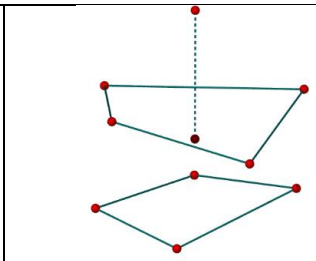
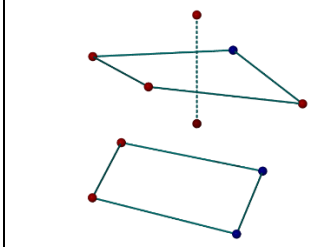
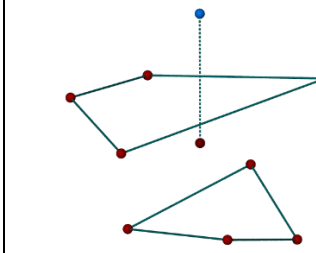
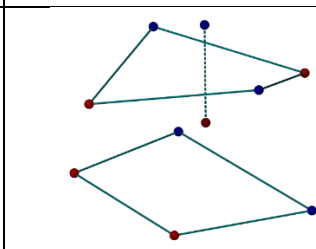
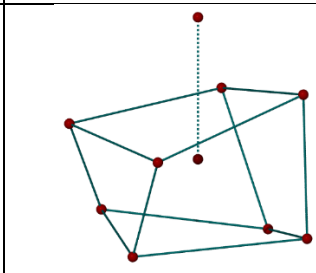
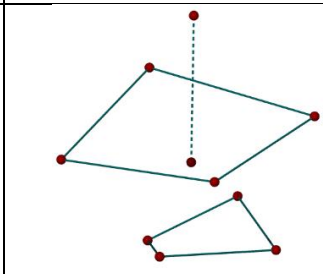
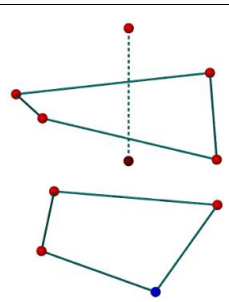
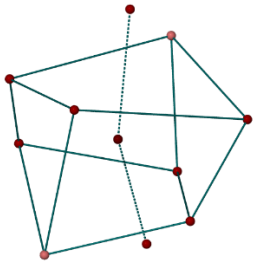
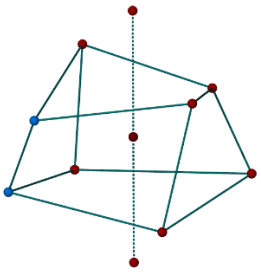
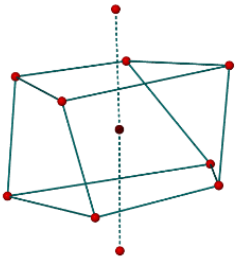
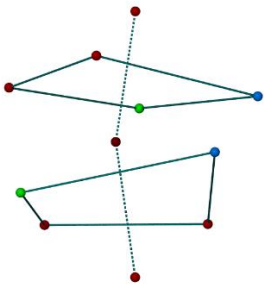
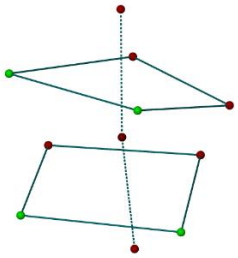
$Pb(C_5H_3N_2O_2)_2$		SAPR-8	Echeverría *et al.*, 2017
$Pb(C_4H_4NO_4S)_2$		SAPR-8	Starosta & Leciejewicz, 2010
$PbI_2(C_{18}H_{14}N_4O)_2$		HBPY-8	Mahmoudi, *et al.*, 2019
$Pb_{2.5}(H_2O)_2(C_8H_6O_4)_2$ Pb at (0, 0, 0)		HBPY-8	Ghosh & Sanguramath, 2008
$Pb(C_4H_2O_4S)$ Pb on two-fold rotation axis		OCT-8	He *et al.*, 2018

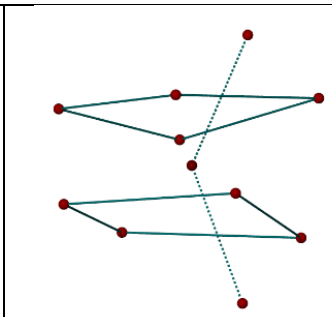
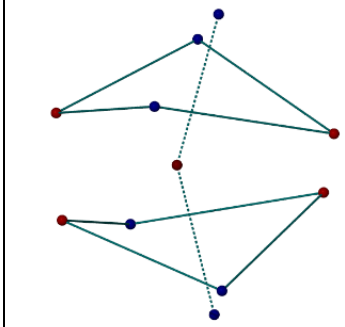
Table S6. Lead(II) coordination assigned as 9- and 10-vertex polyhedral (stereochemically-inert lone pair)

Pb(II) compound		**IUPAC**	**Ref.**
$Pb_2(NO_3)_2(C_{12}H_{10}N_4O)\cdot 2ClO_4$		TRPS-9	Mahmoudi *et al.*, 2019
$Pb_2(H_2O)(C_{26}H_{20}N_6O_2)_4\cdot ClO_4$		TRPS-9	
$[Pb2(C_{21}H_{23}N_7O_2)_2(CF_3O_3S)3]\cdot(CF_3O_3S)\cdot C_2H_3N$ Pb at (0.3822, 0.6267, 0.8662)		TRPS-9	Lobo *et al.*, 2019
$Pb(H_2O)(C_{10}H_8N_2)(C_7H_4O_6S)$		SAPRS-9	Imran *et al.*, 2015
$Pb_5(C_8H_3F_2O_4)_4(C_7H_4FO_2)_2$ Pb at (1.0696, 0.8235, -0.0581)		SAPRS-9	Song *et al.*, 2014
$Pb_2(H_2O)(C_{10}H_8N_2)(C_8H_3F_2O_4\cdot 3H_2O$ Pb at (0.4827, 0.5741, 0.1937)		SAPRS-9	

			
$Pb(H_2O)(NO_3)_2(C_{10}H_9ClON_6O_2)\cdot H_2O$		SAPRS-9	Deng *et al.*, 2013
$Pb_2Cd(NO_3)_6(C_{10}H_8N_2)_2$ Pb at (0.5362, 0.3732, 0.4164)		SAPRS-9	Najafi *et al.*, 2018
$Pb_2Cd(NO_3)_6(C_{10}H_8N_2)_2$ Pb at (0.8543, 0.1384, 0.0811)		SAPRS-9	
$Pb_4(H_2O)(C_5H_4NO_2)_8$ Pb at (0.3051, 0.6932, 0.6134)		SAPRS-9	Kowalik *et al.*, 2017
$Pb(H_2O)(NO_3)_2(C_{12}H_8N_2)$		SAPRS-9	Zhao *et al.*, 2007

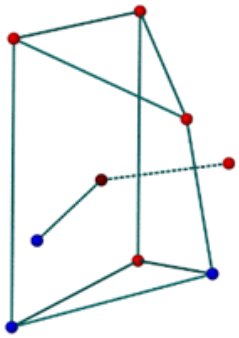
$Pb_2(C_9H_3O_6)(C_9H_4O_6)\cdot 2H_2O$ Pb at (0.0864,0.0872,0.6115)		SAPRS-9	Hayati *et al.*, 2018
$Pb(NO_3)_2(H_2O)_2(C_{19}H_{13}N_5)\cdot C_{19}H_{13}N_5\cdot H_2O$		SAPRS-9	Morsali & Mahjoub, 2004
$[Pb(H_2O)(BF_4)(C_{12}H_{24}O_6)]_2\cdot 2BF_4$		SAPRS-9	Farin *et al.*, 2013
$[Pb_2(C_{37}H_{51}N_{15}O_4)(CF_3O_3S)_4]\cdot CF_3O_3S\cdot C_4H_{10}O\cdot 2H_2O$ Pb at (0.4049, -0.1301, 0.1738)		SAPRS-9	Lobo *et al.*, 2019
$Pb(NO_3)_2(C_{10}H_{20}O_5)$		CUS-9	Farin *et al.*, 2013
$Pb(H_2O)(C_{16}H_{10}O_7)\cdot H_2O$		CUS-9	Yang *et al.*, 2019

$Pb(C_{21}H_{23}NO_6)_2{\cdot}2ClO4{\cdot}C_2H_3N{\cdot}H_2O$		CUS-9	Németh *et al.*, 2015
$Pb(NO_3)_2(C_{12}H_{24}O_4Se_2)$		CUS-10	Farin *et al.*, 2013
$Pb(H_2O)_{1.6}(C_{12}H_{24}O_6)]{\cdot}2PF_6{\cdot}H_2O$		CUS-10	
$[Pb(C_{10}H_{20}O_5)_2[SbCl_6]{\cdot}[SbCl_3(C_{10}H_{20}O_5)]$		CUS-10	von Armin *et al.*, 1993
$Pb(H_2O)_2(BF_4)(C_{12}H_{24}O_4S_2){\cdot}BF_4$		SAPRS-10	Farin *et al.*, 2013
$Pb(C_{10}H_{20}O_3S_2)_2{\cdot}2BF_4{\cdot}CH_2Cl_{21.22}$		SAPRS-10	

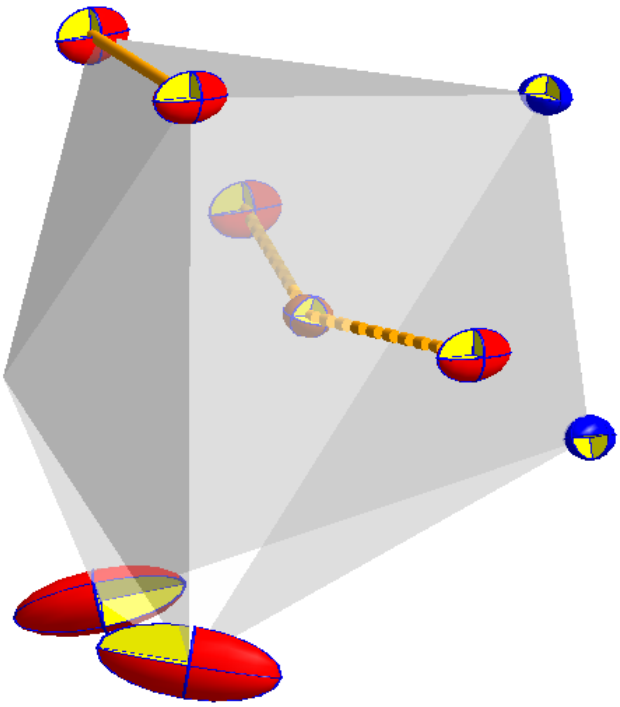
$[(C_4H_9)_4N]_3[Pb(NO_3)_5]$		SAPRS-10	Asanbaeva *et al.*, 2021
$[Pb(ClO_4)(NO_3)(C_{24}H_{16}N_6)$		SAPRS-10	Morsali & Ramazani, 2005

Appendix 1. Divining the position of the lone-pair electron occupying a capping site of a *Ψ*–tricapped trigonal prism

Example $Pb(ClO_4)(C_{12}H_8N_2)(C_2H_3O_2)$ (Hall *et al.*, 2000) from Table S4

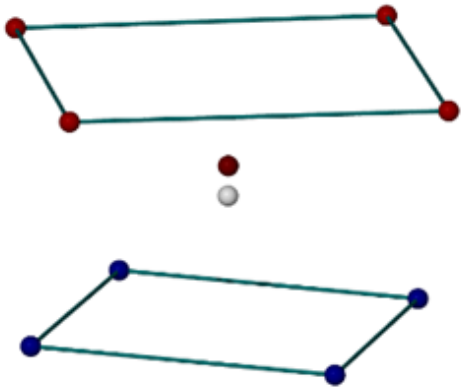


The lone pair is presumed to be located over a near flat O_3N rectangle. The centroid of the O_6N_2 polyhedron is the site of Pb itself, and is 1.364 Å from the O_3N rectangle. The lone pair is then estimated at 1.236 Å above this rectangle so that the Pb—$E_{lone\ pair}$ distance would be 2.60 Å; its position is (-0.2679, 0.2439, -0.1372). The centroid of the nonahedron is also coincident with Pb.



Appendix 2. Divining the position of the lone-pair electron occupying the capping site of a *Ψ*–monocapped square antiprism

Example $Pb(NO_3)_2(C_{16}H_{32}N_8O_4)\cdot 3.5H_2O$ (Cuenot *et al.*, 2008) from Table S4



Pb–centroid 0.295 Å

The coordinates of the centroid of the 4 oxygen—4 nitrogen polyhedron as calculated by using the *XP* graphics software of Bruker's APEX package is (0.1797, 0.0993, -0.1947). The mid-point of the larger square that made by the 4 oxygen atoms is at (0.1839, 0.0518, -0.1953). The distance from Pb to this mid-point square is 0.964 Å. A carbon atom is set at this site.

Assume the lone pair to be 2.60 Å from Pb, and on the opposite of this O_4 square.

In a zero-cycle SHELXL refinement run, the centroid (atom) is connected to Pb, so that an **AFIX 163 1.635** command written in the **ins** input after this arbitrary C atom generates a hydrogen atom at a distance of 2.60 Å from Pb. The lone pair is then assumed as the atom generated this way at (0.1908, -0.0100, -0.1954).

With 8 real atoms and one imaginary lone pair, the new centroid is coincident with Pb; other Pb—$E_{\text{lone pair}}$ distances lead to some divergence of the centroid from Pb.