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crystal X-ray diffraction and ²⁰⁷Pb solid-state NMR spectroscopy study[†]

-diphosphine adducts of $(2,6-Me_2C_6H_3S)_2Pb$: a single

Aaron J. Rossini,^a Alan W. Macgregor,^a Anita S. Smith,^b Gabriele Schatte,^c Robert W. Schurko^{*a} and Glen G. Briand^{*b}

Structural variation in ethylenediamine and

Coordination complexes of $(2,6-Me_2C_6H_3S)_2Pb$ (1) with flexible bidentate ligands have been prepared to explore new bonding environments for Pb(II) thiolates. The reaction of 1 with a series of ethylenediamine and ethylenediphosphine ligands resulted in isolation of the adducts $[(2,6-Me_2C_6H_3S)_2Pb]_2$ (tmeda) (9), $[(2,6-Me_2C_6H_3S)_2Pb]_3(dmpe)$ (10) and $[(2,6-Me_2C_6H_3S)_2Pb]_2(dppe)$ (11) [tmeda = $N_iN_iN'_iN'_i$ -tetramethylethylenediamine; dmpe = bis(dimethylphosphino)ethane; dppe = bis(diphenylphosphino)ethane]. The X-ray crystal structure of **9** shows a dinuclear species in which tmeda is chelating a ψ -trigonal bipyramidal S_2N_2 Pb centre via axial and equatorial sites. The structure of **10** displays a trinuclear structural unit in which dmpe is chelating a ψ -trigonal bipyramidal S₂P₂ Pb centre via equatorial sites. Compounds **9** and 10 also contain a second unique metal centre with ψ -tetrahedral S₃Pb bonding motifs. The structure of 11 shows the dppe ligand bridging two Pb ψ -tetrahedral S₂P metal bonding environments. Static ²⁰⁷Pb solid-state NMR (SSNMR) spectra of 9-11 and [Ph₄As][(PhS)₃Pb] (12) were acquired with cross polarization (CP)-CPMG and frequency swept pulse (WURST)-CPMG pulse sequences, and the efficiencies of these pulse sequences are compared. The ²⁰⁷Pb SSNMR spectra reveal that the lead chemical shift anisotropies (CSA) vary greatly between the different Pb sites, and are generally large in magnitude. DFT calculations are utilized to relate the orientations of the ²⁰⁷Pb nuclear magnetic shielding tensors to the molecular structures, and to aid in spectral assignment where multiple Pb centres are present. The combination of X-ray diffraction, ²⁰⁷Pb SSNMR and DFT is shown to be invaluable for the structural characterization of these important structural motifs, and should find wide-ranging application to numerous lead coordination compounds.

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Introduction

The study of weak dative bonding interactions and metal bonding environments has emerged as an important field of

study over the past number of years.¹⁻⁶ This is a result of the exploitation of these interactions for the self-assembly of supramolecular structures with useful physical properties. Heavy p-block metals, such as Pb(II), are potentially diverse coordination centers for such systems.⁷⁻¹³ For example, the large atomic radius of Pb(II) allows high coordination numbers for the element, while the number of possible bonding environments is augmented by the variable stereochemical activity of its valence lone pair.^{11,13-16} The preference for high coordination numbers typically manifests itself in the formation of polymeric species, as is observed in the solid-state structures of the $Pb(\pi)$ thiolates $[(RS)_2Pb]_4$ (R = C₆H₅, 4-MeC₆H₄, CH₂)¹⁷⁻²⁰ via extensive intermolecular Pb...S interactions.²¹⁻²⁴ Unfortunately, this results in inherent insolubility in these compounds,²⁵ which has delayed the development of their structural chemistry.

In light of this, we previously reported the preparation of the 2,6-dimethylphenylthiolate (2,6-Me_2C_6H_3S)_2Pb (1), which

^aDepartment of Chemistry and Biochemistry, University of Windsor, Windsor, Ontario, Canada N9B 3P4. E-mail: rschurko@uwindsor.ca; Fax: +1 (519) 973-7098; Tel: +1 (519) 253-3000 ext 3548

^bSaskatchewan Structural Sciences Centre, University of Saskatchewan, Saskatoon, Saskatchewan, Canada S7N 5C9. E-mail: gbriand@mta.ca; Fax: +1 (506) 364-2313; Tel: +1 (506) 364-2346

^cDepartment of Chemistry and Biochemistry, Mount Allison University, Sackville, New Brunswick, Canada E4L 1G8

[†]Electronic supplementary information (ESI) available: X-ray crystallographic data for **9–11** in CIF format, complete details of ²⁰⁷Pb SSNMR experiments, experimental and simulated MAS ²⁰⁷Pb SSNMR spectra of **9** and **12** and a powder X-ray diffraction pattern of **10**. CCDC 827117 (**9**), 827118 (**10**) and 827119 (**11**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt33070b

shows an increased solubility in organic solvents over the alkyl- and unsubstituted arylthiolate (RS)₂Pb analogues.²⁶ Reaction of 1 with pyridine (py) yielded the 1:2 adduct (2,6- $Me_2C_6H_3S_2Pb(py)_2$ (2), which is monomeric and exhibits no intermolecular Pb-S contacts.²⁶ Further, bridging Lewis base ligands 4,4'-bipyridyl (bipy) and pyrazine (pyr) afforded the 1:1 coordination polymers $[(2,6-Me_2C_6H_3S)_2Pb(L)]_4$ [L = bipy (3), pyr (4)].²⁶ Interestingly, all complexes show a trigonal bipyramidal S₂N₂ coordination geometry, with the thiolate sulfur atoms occupying equatorial positions (Chart 1). The axial amine nitrogen atoms are involved in dative bonding interactions with the $[(2,6-Me_2C_6H_3S)_2Pb]$ unit, presumably through the empty valence p-orbital of the Pb(II) centre. A similar bonding situation has also been described for (H₂NCH₂CH₂S)₂Pb (5), which involves intramolecular S-N bonding interactions via chelating aminoethane thiolate ligands.27,28

To further manipulate the lead bonding environments, we have also previously investigated the influence of systematically altering the Lewis basicity of the coordinating pyridine ligands.²⁹ This resulted in the isolation of dimeric [(2,6-Me₂C₆H₃S)₂Pb(pyCHO)]₂ (6) and [(2,6-Me₂C₆H₃S)₂Pb(pyOMe)]₂ (7), which feature novel S₃N ψ -trigonal bipyramidal coordination environments, and monomeric [(2,6-Me₂C₆H₃S)₂Pb(pyNMe)] (8), which features a S₂N ψ -tetrahedral bonding environment (pyCHO = 4-pyridinecarboxaldehyde, pyOMe = 4-methoxypyridine, pyNMe₂ = 4-dimethylaminopyridine). Like 2–5, dative Pb–N (and Pb–S) bonding interactions in 6 and 7 also occur at *axial* coordination sites, with the thiolate sulfur atoms occupying equatorial positions.³⁰

Owing to the insolubility of many of these lead thiolate complexes, ²⁰⁷Pb solid-state NMR (SSNMR) has proven to be useful for their structural characterization. It is well known that ²⁰⁷Pb SSNMR is a useful probe of molecular and electronic structure for lead containing materials,^{29,31–39} and is also very useful for confirming that the bulk sample is representative of

single crystals isolated for characterization by X-ray diffraction techniques. We have previously applied ²⁰⁷Pb SSNMR to characterize complexes 2, 7 and 8.²⁹ With the aid of DFT calculations of lead magnetic shielding (MS) tensors we have previously demonstrated that the large lead CSAs arise from the presence of stereochemically active electron lone pairs, and that the lead MS tensor orientations are highly dependent upon the orientation of the lone pair with respect to the molecular frame. While this combined strategy represents a powerful probe of structure for lead complexes, acquisition of solidstate ²⁰⁷Pb NMR spectra is often very challenging because of the CSA induced broadening of the 207Pb powder patterns which often exceeds 2000 ppm. For example, previous spectral acquisitions were often very time-consuming (>24 hours), despite being acquired with a ¹H-²⁰⁷Pb cross polarization/ Carr-Purcell Meiboom Gill (CP/CPMG) pulse sequence for signal enhancement. For complexes lacking protons these issues could be exacerbated since it would not be possible to apply cross polarization and the longitudinal relaxation times of lead (and other heavy element nuclides) are highly variable $(1 \text{ s} < T_1(^{207}\text{Pb}) < 160 \text{ s}).^{31,40-42}$ One possibility for accelerating acquisition of ²⁰⁷Pb solid-state NMR spectra would be to apply the wideband uniform rate smooth truncation (WURST)-CPMG pulse sequence, possibly in combination with frequencystepped acquisitions (i.e., variable-offset cumulative spectra, VOCS).43-45

In order to impose dative bonding at *equatorial* coordination sites, adducts of **1** which incorporate flexible bidentate ethylenediamine and diphosphine ligands have been prepared. This has resulted in isolation of the complexes [(2,6-Me₂C₆H₃S)₂Pb]₂(tmeda) (9), [(2,6-Me₂C₆H₃S)₂Pb]₃(dmpe) (10) and [(2,6-Me₂C₆H₃S)₂Pb]₂(dppe) (11) [tmeda = N,N,N',N'-tetramethylethylenediamine; dmpe = bis(dimethylphosphino)-ethane; dppe = bis(diphenylphosphino)ethane]. The various novel Pb(π) bonding environments and structural motifs of **9–11** have been probed by X-ray crystallographic analysis, ²⁰⁷Pb



 $R = 2,6-Me_2C_6H_3$

Chart 1 Schematic drawings of the solid-state structures of complexes 2–11.

solid-state NMR and DFT calculations. ²⁰⁷Pb SSNMR spectra of **9–11** and $[Ph_4As][(PhS)_3Pb]$ (**12**) were acquired in a piecewise fashion with the CP/CPMG pulse sequence. The WURST-CPMG pulse sequence was also used to obtain the ultra-wideline (UW) ²⁰⁷Pb SSNMR spectra in a single experiment. Total experiment times for spectra acquired with CP/CPMG and WURST-QCPMG are compared in order to determine the most efficient method for acquiring UW ²⁰⁷Pb SSNMR spectra for these systems. DFT calculations were carried out in order to determine the MS tensor orientations and relate the experimentally observed CS parameters to the molecular structures.

Experimental

General considerations

2,6-Dimethylbenzenethiol 95%, 1,2-bis(diphenylphosphino)ethane 97%, 1,2-bis(dimethylphosphino)ethane 97% and *N*,*N*, *N'*,*N'*-tetramethylethylenediamine 99.5%+ (redistilled) were used as received from Aldrich. Lead(II) acetate trihydrate was used as received from Fisher. $(2,6-Me_2C_6H_3S)_2Pb$ (1)^{22,23} and [Ph₄As][(PhS)₃Pb] (12)⁴⁶ were prepared according to previously reported procedures. All reactions were carried out under an atmosphere of dinitrogen using standard Schlenk techniques.

Solution ¹H, ¹³C{¹H} and ³¹P{¹H} NMR spectra were recorded on a JEOL GMX 270 MHz spectrometer (270.2, 67.9 and 109 MHz, respectively) or a Varian MERCURY 200 MHz + spectrometer (200.0, 50.3 and 81.0 MHz, respectively), and chemical shifts are calibrated to the residual solvent signals. FT-IR spectra were recorded as Nujol mulls on a Mattson Genesis II FT-IR spectrometer in the range 4000–400 cm⁻¹. Melting points were recorded on an Electrothermal MEL-TEMP melting point apparatus and are uncorrected. Elemental analyses were performed by Chemisar Laboratories Inc., Guelph, Ontario.

Preparation of [(2,6-Me₂C₆H₃S)₂Pb]₂(tmeda) (9). Tmeda (0.099 g, 0.83 mmol) was added dropwise to a yellow slurry of 1 (0.200 g, 0.415 mmol) in toluene (3 mL). After 10 min, the reaction mixture was filtered, layered with hexane (1 mL) and allowed to stand at 4 °C. After 3 d, the reaction was filtered to yield yellow crystals of 9 (0.188 g, 39%). Anal. Calcd for [(2,6-Me₂C₆H₃S)₂Pb]₂(tmeda): C, 46.13; H, 5.17; N, 2.39. Found: C, 41.55; H, 5.05; N, 2.59%. Mp 144-146 °C (d). FT-IR (cm⁻¹): 586 w, 669 m, 758 s, 787 m, 947 m, 1022 m, 1051 s, 1160 w, 1244 vw, 1286 w, 1527 m, 1579 w, 2723 w, 3045 m. NMR data (dmso-d₆): ¹H NMR, $\delta = 2.27$ [s, 12H, (Me₂N)₂C₂H₄], 2.40 (s, 24H, $C_6H_3Me_2$), 2.51 [s, 4H, $(Me_2N)_2C_2H_4$], 6.68 (t, ${}^3J_{HH}$ = 7 Hz, 4H, p-C₆ H_3 Me₂), 6.95 (d, ${}^{3}J_{HH} = 7$ Hz, 8H, m-C₆ H_3 Me₂); 13 C{¹H} NMR, $\delta = 24.19$ (C₆H₃Me₂), 46.09 [(Me₂N)₂C₂H₄], 57.74 $[(Me_2N)_2C_2H_4]$, 123.78 $(C_6H_3Me_2)$, 126.81 $(C_6H_3Me_2)$, 141.43 $(C_6H_3Me_2)$, 142.19 $(C_6H_3Me_2)$.

Preparation of $[(2,6-Me_2C_6H_3S)_2Pb]_3(dmpe)$ (10). Dmpe (0.128 g, 0.852 mmol) was added dropwise to a slurry of 1 (0.194 g, 0.123 mmol) in toluene (3.5 mL). After 10 min, the reaction mixture was filtered, layered with hexane (2 mL) and

allowed to stand at 4 °C. After 1 d, the reaction was filtered to yield yellow crystals of **10** (0.077 g, 11%). Anal. Calcd for [(2,6-Me₂C₆H₃S)₂Pb]₃(dmpe): C, 40.63; H, 4.43; N, 0.00. Found: C, 41.37; H, 4.66; N, <0.20%. Mp 152–155 °C (d). FT-IR (cm⁻¹): 584 vw, 762 s, 891 w, 945 s, 1049 m, 1157, w, 1302 w, 1558 vw, 2605 vw, 2665 w, 2725 m, 3190 w. NMR data (dmso-d₆): ¹H NMR, δ = 1.16 [s, 12H, (*Me*₂P)₂C₂H₄], 1.53 [m, 4H, (Me₂P)₂C₂H₄], 2.42 (s, 36H, C₆H₃*Me*₂), 6.69 (t, ³*J*_{HH} = 7 Hz, 6H, *p*-C₆*H*₃Me₂), 6.95 (d, ³*J*_{HH} = 7 Hz, 12H, *m*-C₆*H*₃Me₂); ¹³C{¹H} NMR, δ = 13.24 [(*Me*₂P)₂C₂H₄], 24.37 (C₆H₃*Me*₂), 27.34 [(Me₂P)₂C₂H₄], 124.01 (*C*₆H₃Me₂), 126.97 (*C*₆H₃Me₂), 141.41 (*C*₆H₃Me₂), 142.34 (*C*₆H₃Me₂); ³¹P{¹H} NMR, δ = -34.47.

Preparation of [(2,6-Me₂C₆H₃S)₂Pb]₂(dppe) (11). A solution of dppe (0.167 g, 0.402 mmol) in toluene (2 mL) was added to a slurry of (0.100 g, 0.208 mmol) in toluene (3 mL) to give a cloudy orange solution. After 15 min, the red-orange solution was filtered and left at 4 °C. After 3 d, the reaction mixture was filtered to yield small yellow crystalline blocks of 11 (0.077 g, 31%). Anal. Calcd for [(2,6-Me₂C₆H₃S)₂Pb]₂(dppe): C, 58.91; H, 5.13; N, 0.00. Found: C, 54.53; H, 4.54; N, <0.05%. Mp 150-152 °C (d). FT-IR (cm⁻¹): 503 m, 570 w, 692 s, 733 s, 771 s, 847 vw, 1024 w, 1051 m, 1095 w, 1159 w, 1273 w, 1309 w, 2669 w, 2723 w, 3043 w. NMR data (dmso-d₆): ¹H NMR, δ = 2.03 [m, 4H, $(Ph_2P)_2C_2H_4$], 2.43 (s, 24H, $C_6H_3Me_2$), 6.69 (t, ${}^{3}J_{\text{HH}}$ = 7 Hz, 4H, *p*-C₆H₃Me₂), 6.98 (d, ${}^{3}J_{\text{HH}}$ = 7 Hz, 8H, m-C₆ H_3 Me₂), 7.29 [m, 20H, (Ph_2 P)₂C₂H₄]; ¹³C{¹H} NMR, δ = 23.78 $[(Ph_2P)_2C_2H_4]$, 24.34 $(C_6H_3Me_2)$, 123.99 $(C_6H_3Me_2)$, 126.92 ($C_6H_3Me_2$), 129.31 [(Ph_2P)₂ C_2H_4], 133.01 [(Ph_2P)₂ C_2H_4], 138.36 [$(Ph_2P)_2C_2H_4$], 141.33 ($C_6H_3Me_2$), 142.35 ($C_6H_3Me_2$); ³¹P{¹H} NMR, $\delta = -13.40$.

X-ray structural analysis

Crystals of 9-11 were isolated from the reaction mixtures as indicated above. Single crystals of each compound were coated with Paratone-N oil, mounted using a CryoLoop (Hampton Research) and frozen in the cold stream of the goniometer. Data were measured on a Bruker AXS/Nonius KappaCCD 4-Circle Kappa FR540C diffractometer using monochromated Mo K_{α} radiation (l = 0.71073 Å) at -100 °C. Data were collected using φ and/or ω scans.⁴⁷ Data reduction was performed with the HKL DENZO and SCALEPACK software, which corrects for beam inhomogeneity, possible crystal decay, Lorentz and polarisation effects. A multi-scan absorption correction was applied (SCALEPACK).48 Transmission coefficients were calculated using SHELXL97-2.49 The structures were solved by direct methods (9, 11) or the heavy atom method (10) (SHELXS-97)⁵⁰ refined by full-matrix least squares on F^2 and (SHELXL-2012).49 The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically idealized positions (C–H bond distances 0.95/0.99 Å) and were not refined. The isotropic thermal parameters of the hydrogen atoms were fixed at 1.2 times that of the preceding carbon atom.

In the structure of **9** the carbon atoms of the CH_2 -groups [labelled C(1A), C(2A), C(1B) and C(2B)] in the TMEDA ligand were disordered over two positions with refined site-occupancy

factors of 0.620(14) and 0.380(14), respectively. In the structure of (10) approximately 23% of the unit cell volume (1576 $Å^3$) comprises a region of disordered solvent which could not be modeled as discrete atomic sites. The program PLATON/ SQUEEZE⁵¹ was used to calculate the contribution from the solvent region to the diffraction. A total electron count of 148 electrons was found in the total solvent-accessible void volume within the unit cell. The electron count of 74 e⁻/void corresponds to 1.5 molecules of toluene in each void. Toluene was used as a solvent for growing the crystals. The data were then corrected for disordered electron density leading to a set of solvent-free diffraction intensities. The modified data improved the *R*-factors (before SQUEEZE: $R_1 = 0.0361$, w $R_2 =$ 0.1009; after SQUEEZE: $R_1 = 0.0316$, $wR_2 = 0.0743$). Derived values (formula weight, density, absorption coefficient) do not contain the contribution of the disordered solvent. The carbon atoms [labelled C(41A), C(42A), C(43B), C(41B), C(42B) and C(43B)] in the dmpe ligand of 10 were disordered over two sites. The site-occupancy factors were allowed to refine and converged to 0.65 and 0.35, respectively.

Solid-state NMR

Solid-state ²⁰⁷Pb spectra were acquired on a Varian Infinity Plus spectrometer with an Oxford 9.4 T wide-bore magnet (ν_0 (¹H) = 400 MHz, ν_0 (²⁰⁷Pb) = 83.74 MHz). Lead chemical shifts were referenced to tetramethyllead (Pb(CH₃)₄, δ_{iso} = 0.0 ppm) by using a 0.5 M aqueous solution of Pb(NO₃)₂ (δ_{iso} = -2941 ppm) as a secondary standard.³⁸

Solid-state NMR experiments were carried out using either a 4 mm HX double resonance Varian/Chemagnetics probe or a 4 mm HXY triple resonance Varian/Chemagnetics probe. Lead acetate hydrate [Pb(OAc)₂·xH₂O] was used to optimize parameters for cross polarization/Carr-Purcell-Meiboom-Gill (CP/ CPMG)^{32,52} and WURST-CPMG^{53,54} experiments. The total spectrum for each CP/CPMG experiment was obtained by coadding individual sub-spectra that were collected at evenly spaced transmitter offsets of 20 or 24 kHz. Other experimental details regarding CP/CPMG experiments can be found in the ESI (Table S1[†]). TPPM ¹H decoupling was used for all experiments.55 WURST-CPMG experiments were able to be completed without piecewise acquisition and employed 50 µs WURST pulses with a pulse power of ca. 47 kHz. Further experimental details regarding WURST-CPMG experiments also may be found in the ESI.[†] All ²⁰⁷Pb spectra were simulated using the WSolids NMR simulation program,⁵⁶ and processed with the NUTS computer program (Acorn NMR).

DFT calculations

The NMR and EPR modules^{57–59} of the *Amsterdam Density Functional* (ADF) program package^{60–62} running on the Shared Hierarchical Academic Research Computing Network (SHARC-NET) were used to carry out all theoretical calculations. Relativistic effects were accounted for using the zeroth-order regular approximation (ZORA).^{63–67} All-electron gauge including atomic orbitals (GIAO)⁶⁸ triple- ζ doubly-polarized basis sets were used for all atoms, except for the Pb atom(s) in each

structure for which a quadruple- ζ doubly polarized basis set was employed. All calculations were carried out with complete molecular units (except for those mentioned below) using atomic coordinates from single-crystal X-ray experiments, however, the position of H atoms were corrected by setting C-H bond lengths to more realistic values of 1.09 Å. For **12**, the Ph₄As⁺ cation was excluded and calculations were performed on a single negatively charged (PhS)₃Pb unit. For **11**, only one Pb unit was employed for calculations. This was accomplished by replacing the second phosphine atom with a hydrogen atom and removing the other lead and thiolate ligand atoms.

Results and discussion

The persistence of a ψ -trigonal bipyramidal S_2N_2 coordination geometry for Pb(II) in which py (2), bipy (3) and pyr (4) adducts of (2,6-Me₂C₆H₃S)₂Pb occupy *trans* axial coordination sites^{26–28} has prompted us to study the effect of tethering the donor atoms *via* a flexible backbone. This allows for the possibility of chelation of the metal centre *via cis*-coordination sites and the isolation of novel Pb(II) bonding environments. Ethylenediamine and diphosphine ligands were chosen as they allow for the formation of favourable five-membered chelate rings.^{27,28} Further, structurally characterized adducts of neutral diphosphine ligands with Pb(II) centers have not been previously reported.

Syntheses

Reaction of $(2,6-Me_2C_6H_3S)_2Pb$ (1) with an excess of the appropriate ethylenediamine or diphosphine ligand in toluene yielded products which exhibit varying metal-ligand ratios. Reaction with two equivalents of tmeda yielded the 2:1 adduct $[(2,6-Me_2C_6H_3S)_2Pb]_2$ (tmeda) (9), while reaction with seven equivalents of the diphosphine analogue dmpe resulted in isolation of the 3:1 complex [(2,6-Me₂C₆H₃S)₂Pb]₃(dmpe) (10). Finally, reaction with two equivalents of the bis(diphenylphosphine) analogue yielded the 2:1 adduct [(2,6- $Me_2C_6H_3S_2Pb_2(dppe)$ (11). All products were isolated in low to moderate yields, and were the only crystalline materials isolated from a number of reactions involving various (2,6-Me₂C₆H₃S)₂Pb: ligand ratios. Although satisfactory elemental analysis could not be obtained for compounds 9 and 11, the products were spectroscopically and structurally characterized (vide infra).

Solution NMR studies

Solution ¹H and ¹³C{¹H} NMR spectra of adducts **9–11** in dmso-d₆ generally show similar resonances to those observed for **1**²⁶ and the corresponding ethylenediamine/-diphosphine ligands in the same solvent. Interestingly, the tmeda (**9**: δ 2.27 and 2.51) and dmpe (**10**: δ 1.16 and 1.53) ¹H NMR signals in these complexes show slight shifts from those of the respective uncomplexed ligands (tmeda: δ 2.11 and 2.27; dmpe: δ 0.96 and 1.36). The ³¹P{¹H} NMR spectrum of **10** also shows a shift in the phosphorus signal (δ –33.88) from that of the free dmpe

ligand (δ –47.55). This suggests weak Pb–N and Pb–P interactions in dmso-d₆ solution for 9 and 10, respectively. Interestingly, the solution ¹H, ¹³C{¹H} and ³¹P{¹H} NMR spectra of 11 show no shifts from those of the free dppe ligand in dmso-d₆. These data are consistent with previous observations for 2–8, in which solution ¹H, ¹³C and ²⁰⁷Pb NMR data showed the complexes to be quite labile in solution.^{26,29} The structures, therefore, do not persist and can be studied only in the solid state.

X-ray structural analyses

Crystals suitable for X-ray crystallographic analysis were isolated for **9–11** by the slow evaporation of reaction mixtures at 23 °C. Crystallographic data is given in Table 1. Selected bond distances and angles are given in Tables 2–4.

The X-ray crystal structure of **9** (Fig. 1) shows a dinuclear unit containing two unique Pb centers. Pb1 is four coordinate,

	9 ⋅C ₇ H ₈	10	11
Formula	$C_{45}H_{60}N_2Pb_2S_4$	$C_{54}H_{70}P_2Pb_3S_6$	$C_{58}H_{60}P_2Pb_2S_4$
FW	1171.57	1594.97	1181.48
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	<i>P</i> 1̄ [No. 2]	C2/c [No. 15]	<i>P</i> 1 [No. 2]
a (Å)	11.9125(1)	20.2754(2)	10.0551(2)
b (Å)	14.0434(2)	20.1016(2)	11.3774(2)
c (Å)	14.9513(2)	18.9169(2)	12.8875(3)
α (°)	99.7056(8)	90	87.0455(9)
$\beta(\circ)$	109.47205(8)	114.6800(6)	71.5348(10)
γ (°)	90.8606(8)	90	81.6016(7)
$V(Å^3)$	2317.58(5)	7005.65(13)	1383.42(5)
Z	2	4	1
F(000)	1144	3064	666
ρ_{calcd} (g cm ⁻³)	1.679	1.512	1.634
$\mu (\text{mm}^{-1})$	7.467	7.444	6.321
$T(\mathbf{K})$	173(2)	173(2)	173(2)
Λ (Å)	0.71073	0.71073	0.71073
R_1^{a}	0.0236	0.0316	0.0381
wR_2^b	0.0506	0.0743	0.0766

Table 2 Selected bond distances (Å) and angles (°) for 9.C7H8

Pb1–N1 Pb1–N2 Pb1–S1	$9 \cdot C_7 H_8$
Pb1-N2 Pb1-S1	2.455(2)
Pb1-S1	2.632(3)
	2.5880(8)
Pb1-S2	3.0276(8)
Pb2-S2	2.7027(8)
Pb2-S3	2.6172(8)
Pb2-S4	2.6257(8)
N1-Pb1-N2	71.94(9)
S1-Pb1-S2	97.12(2)
S1-Pb1-N1	89.57(7)
S1-Pb1- N2	93.16(7)
S2-Pb1-N1	85.28(6)
S2-Pb1-N2	154.91(7)
S2-Pb2-S3	99.62(2)
S4-Pb2-S2	89.42(2)
S3-Pb2-S4	96.07(3)

Table 3	Selected	bond	distances	(Å)	and	angles	(°)) for 1	0
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	10
Pb1-P1	2.8389(10)
Pb1-S1	2.9869(9)
Pb2-S1	2.7385(9)
Pb2-S2	2.6430(12)
Pb2-S3	2.6839(10)
P1-Pb1-P1*	73.49(5)
S1-Pb1-S1*	154.15(4)
S1-Pb1-P1	77.91(3)
S1-Pb1-P1*	81.42(3)
S1-Pb2-S2	84.99(4)
S1-Pb2-S3	84.38(3)
S2-Pb2-S3	95.43(4)

Table 4 Selected bond distances (Å) and angles (°) for 11

	11
Pb1-S1 Pb1-S2 Pb1-P1	2.6079(13) 2.6171(11) 2.8161(11)
S1–Pb1–S2 S2–Pb1–P1 S1–Pb1–P1	$96.86(4) \\ 86.84(3) \\ 85.43(4)$



Fig. 1 X-ray structure of ${\bf 9}$ (30% probability ellipsoids). Hydrogen atoms are removed for clarity.

and is bonded to two nitrogen atoms of a chelating tmeda ligand [Pb1–N1 2.455(2) and Pb1–N2 2.632(3) Å] and two thiolate sulfur atoms [Pb1–S1 2.5880(8) and Pb1–S2 3.0276(8) Å]. If the stereochemically active lone pair is considered, the resulting coordination geometry at Pb1 is distorted ψ -trigonal bipyramidal. Here, both N1 and S1 occupy equatorial positions [S1– Pb1–N1 = 89.57°], while N2 and S2 occupy the axial positions [S2–Pb1–N2, 154.91(7)°]. The Pb1–N2 bond distance is significantly larger than that of Pb1–N1, which is presumably a result of the *trans* influence imposed by the S2 thiolate sulfur atom.^{29,69} The Pb1–N1 bond distance is shorter than those observed in previously reported tmeda adducts of Pb(II) [Pb–N 2.608(44)–2.879(3) Å]],^{70–72} while the Pb1–N2 bond distance is similar. Pb2 is bonded to two terminal thiolate sulfur atoms *via* short Pb–S bonds [2.6172(8) and 2.6257(8) Å], which are comparable to those Pb–S distances observed in the [(PhS)₃Pb]⁻ anion (**12**, Chart 2) [2.619(1)–2.696(3) Å]^{46,73} (*vide infra*). A third thiolate sulfur atom is more weakly bonded [Pb2–S2 2.7027(8) Å], and bridges the two unique Pb centres. This results in a pyramidal coordination geometry for Pb2, which may be described as distorted ψ -tetrahedral if a stereochemically active lone pair is considered. Finally, **9** crystallizes with a non-coordinated toluene molecule in the lattice.

The X-ray structure of compound **10** (Fig. 2) depicts a trinuclear unit with two unique Pb centers. Pb1 is four coordinate, and is bonded by two phosphorus atoms of the chelating dmpe ligand [Pb1–P1 2.8386(10) Å] and two thiolate sulfur



Chart 2 Schematic drawing of the lead coordination environment of complex 12.



atoms [Pb1–S1 2.9870(9) Å)]. The Pb1–P1 bond distance is in the range of those previously reported for complexes involving monodentate phosphine ligands [2.758(2) and 2.884(3) Å].⁷⁴ If a stereochemically active lone pair is considered, the resulting geometry at Pb1 is distorted ψ -trigonal bipyramidal, with the two phosphorus atoms occupying equatorial positions [P1– Pb1–P1* 73.48(5)°] and the two sulfur atoms occupying axial sites [S1–Pb1–S1* 154.14(4)°]. As in compound **9**, Pb2 is coordinated by three thiolate sulfur atoms, two of which are terminal [Pb2–S2 2.6428(12) and Pb2–S3 2.6840(10) Å] and one of which bridges Pb1 and Pb2 [Pb2–S1 2.7387(9) Å]. The bond angles at Pb2 support a distorted ψ -tetrahedral geometry with a stereochemically active lone pair.

The X-ray structure of **11** (Fig. 3) depicts a dinuclear unit with one crystallographically unique Pb center. Pb1 is bonded to two thiolate sulfur atoms [Pb–S1 2.6079(13) and Pb–S2 2.6171(11) Å] and one phosphorus atom of the bridging dppe ligand [Pb1–P1 2.8161(11) Å]. This results in a three-coordinate pyramidal geometry at Pb1, which may be described as distorted ψ -tetrahedral if the stereochemically active lone pair is considered.

Although a comparison of **9** and **10** shows their overall dinuclear and trinuclear structures to be quite different, both exhibit two crystallographically unique Pb centers. Pb1 of both complexes shows a distorted ψ -trigonal bipyramidal coordination geometry, where the metal center is complexed by either a chelating tmeda (**9**) or dmpe (**10**) ligand and two thiolate sulfur atoms. In **9**, however, the atoms of the chelating



Fig. 2 X-ray structure of **10** (30% probability ellipsoids). Hydrogen atoms are removed for clarity. Symmetry transformations used to generate equivalent atoms: (*) -x + 1, $y_r - z + 0.5$.

Fig. 3 X-ray structure of **11** (30% probability ellipsoids). Hydrogen atoms are removed for clarity. Symmetry transformations used to generate equivalent atoms: (*) -x + 1, -y + 1, -z.



Fig. 4 Novel bonding environments for Pb(II) exhibited by compounds (a) 9, (b) 10 and (c) 11.

ligand occupy an axial and an equatorial site, whereas in 10 they occupy two equatorial positions. In our previous work with $Pb(\pi)$ thiolate amine adducts (2-4), the amine ligands occupied axial position of the ψ -trigonal bipyramidal bonding environment in each case.²⁶ Therefore, use of bidentate ligands with flexible ethylene backbones has allowed for equatorial dative bonding interactions and isolation of novel coordination environments at the Pb(II) thiolate center (Fig. 4a and b). Interestingly, the Pb2 center in 9 and 10 shows a three coordinate pyramidal geometry similar to that previously observed in the $[Ph_4As]^+$ and $[n-Pr_4N]^+$ salts of the monomeric tris-thiolate anion [(PhS)₃Pb]^{-.46,73} Unlike the monomeric anion [Ph₄As][(PhS)₃Pb] (12), however, both 9 and 10 exhibit one longer Pb-S_{bridging} bonding interaction, although the Pb2-S_{bridging} bond is significantly shorter than the Pb1-S_{bridging} interaction in both structures.

In order to further our investigation of the dative phosphine-Pb(II) interaction, dppe was employed to determine the effect of changing the size and electron donor abilities of the phosphine substituents. Although dppe and dmpe share the same PCH₂CH₂P backbone, the dppe ligand in **11** bridges two metal centers, while dmpe chelates a single Pb atom in 10. This is possibly a result of steric crowding by the bulkier phenyl substituents on the phosphorus atoms in 11, as indicated by the orientation of the bulky 2,6-dimethylphenylthiolate ligands away from these groups. The Pb1-P1 distance in 10 [2.8386(10) Å] was found to be significantly longer than that in 11 [2.8161(11) Å], while a similar observation was made regarding Pb1-S bond distances [10: 2.9870(9) Å; 11: 2.6079(13) and 2.6171(11) Å]. This is presumed to be mainly a result of the four- versus three-coordinate Pb bonding environments in 10 and 11, respectively. As in 9 and 10, the distorted ψ-tetrahedral S₂P motif in 11 represents a novel bonding environment for Pb(II) (Fig. 4c).

Solid-state ²⁰⁷Pb NMR spectroscopy

In this section, we examine the ²⁰⁷Pb SSNMR spectra of **9**, **10**, **11** and **12**. Before the spectra of the individual complexes and relations to molecular structure are discussed, strategies for acquiring the UW ²⁰⁷Pb SSNMR spectra are briefly summarized. ¹H-²⁰⁷Pb CP/MAS experiments conducted on **12** and **9** yielded incompletely excited spectra, similar to those presented in our previous work on analogous systems (Fig. S1[†]).²⁹ CP/MAS spectra are useful for obtaining accurate measurements of ²⁰⁷Pb isotropic chemical shifts (δ_{iso}); however, they are unsuitable for extracting anisotropic CS tensor parameters, due to non-uniform excitation and variation in spinning sideband intensities which strongly influence the outcomes of Herzfeld–Berger analyses. Hence, all ²⁰⁷Pb SSNMR spectra were acquired from stationary samples in a piecewise fashion using the CP/CPMG and WURST-CPMG pulse sequences.

We have recently demonstrated that the WURST-CPMG sequence can be utilized to acquire UW SSNMR spectra of spin-half nuclei with fewer sub-spectra, or in some cases, with a single experiment.⁷⁵ In line with these previous observations, it is possible to acquire UW SSNMR spectra of complexes 9-12 in a single WURST-CPMG experiment, although long recycle delays are required (90 s) compared to corresponding CP experiments (20–45 s). For comparison, all of the ²⁰⁷Pb SSNMR spectra are pictured in Fig. 5 and total times for WURST-CPMG and CP/CPMG experiments are listed in Table 5. The ²⁰⁷Pb SSNMR static spectra of 11 and 12 were acquired more quickly with the WURST-CPMG pulse sequence than with the CP/CPMG sequence. Although the CP/CPMG pulse sequence yields sub-spectra with superior signal to noise and requires shorter recycle delays, the WURST-CPMG sequence permits the acquisition of the total SSNMR spectrum in a single experiment. In contrast, for 9 and 10 it was found that CP/CPMG experiments were faster than WURST-CPMG experiments. This is due to a combination of increased ¹H-²⁰⁷Pb CP efficiency, decreased ¹H longitudinal relaxation times $[T_1(^1H)]$ and/or increased ²⁰⁷Pb longitudinal relaxation times $[T_1(^{207}\text{Pb})]$ for 9 and 10 as compared to 11 and 12. However, we note that even for cases where WURST-CPMG is less efficient than CP/CPMG, the former eliminates the need for piecewise experiments, and the requirement that personnel be present to set the transmitter and retune the probe between acquisitions of sub-spectra.

It is possible to extract the CS tensor parameters, which include the isotropic shift (δ_{iso}), the span (Ω) and the skew (κ) (see Table 6 for definitions of these parameters in terms of principal components of the CS tensor), by simulating the static ²⁰⁷Pb SSNMR powder patterns. δ_{iso} represents the average chemical shift value that would be observed if the molecule was rapidly tumbling in an isotropic fashion (δ_{iso} is normally what is measured in solution NMR experiments). Ω indicates the breadth of the chemical shift (CS) pattern in ppm, and reports the magnitude of the CSA. Finally, κ is a dimensionless parameter which indicates the degree of axial symmetry of the CS tensor $(-1 < \kappa < +1)$, where $\kappa = +1$ and -1represent the two extremes of axial symmetry). In general, δ_{iso} of all of the compounds are similar, in spite of the large chemical shift range of lead, which is on the order of 18 000 ppm.³¹ The exception is the δ_{iso} for the PbP₂S₂ site of 10, which is distinct from those of the other complexes. Positive κ values and large values of Ω are observed for all of the compounds ($\Omega > 3400$ ppm, except for the PbP₂S₂ site of **10**), consistent with those previously observed by our research group for analogous lead(π) thiolate complexes (2, 7 and 8).²⁹

The ²⁰⁷Pb SSNMR spectra of **12** are discussed first, as this complex contains a single Pb site in a ψ -tetrahedral PbS₃ environment. Similar PbS₃ sites are also observed in binuclear **9** and trinuclear **10**. The static ²⁰⁷Pb spectra of **12** have a



Fig. 5 ¹H-²⁰⁷Pb CP/CPMG (top spectra: A, C, E and G) and ²⁰⁷Pb WURST-QCPMG (bottom spectra: B, D, F and H) SSNMR spectra of **12**, **11**, **9** and **10**. Analytical simulations (solid red traces) are overlaid on the experimental spectra (black traces). For **9** simulations of the two overlapping individual sites are also shown (inlaid, blue and green traces). ²⁰⁷Pb CS tensor parameters obtained from the simulations are listed in Table 6.

WURST-CPMG						
	9	10	11	12		
Compound Pulse sequence	CP/CPMG					
Total experiment time (h)	20.3	22	23	32		
Number of sub-spectra	19	22	23	20		
Transients per sub-spectrum	192	120	120	128		
Pulse delay (s)	20	30	30	45		
Pulse sequence	WURST-CPMG					
Total experiment time (h)	41.6	60	20.2	19		
Number of sub-spectra	1	1	1	1		
Transients per sub-spectrum	1664	2400	808	759		
Recycle delay ^{a} (s)	90	90	90	90		

 $\ensuremath{\text{Table 5}}$ Comparison of experimental times between CP/CPMG and WURST-CPMG

^{*a*} Recycle delays were not optimized for each complex because of the lengthy experimental times required to obtain spectra of reasonable signal to noise.

breadth of *ca.* 280 kHz (Fig. 5). Simulation of a CSA powder pattern which fits the outer manifold of the spikelet spectrum yields the ²⁰⁷Pb chemical shift tensor parameters, $\delta_{iso} = 2750$ ppm, $\Omega = 3400$ ppm and $\kappa = 0.37$. The value of Ω observed for **12** is smaller than those previously observed for the analogous thiolate complexes **2**, **7** and **8** which feature PbS₂N_n (*n* = 1 or 2) coordination environments for which $\Omega > 3900$ ppm.²⁹

The positive value of κ indicates that δ_{33} is the distinct component of the CS tensor (*i.e.*, δ_{11} and δ_{22} are similar in magnitude). Based on the site symmetry, and previous studies of lead coordination compounds by our group and others,^{29,35} it is predicted that δ_{33} , which corresponds to the direction of highest magnetic shielding, is aligned along or near the direction of the electron lone pair. The CS tensor parameters, as well as the orientation of the CS tensor in the molecular frame, are discussed in detail in the theoretical section below.

Compound **11** features a single Pb site which corresponds to a distorted ψ -tetrahedral PbS₂P environment. The ²⁰⁷Pb NMR spectra of **11** reveal a span of 4400 ppm and skew of 0.48. This span is larger than that measured for the PbS₃ sites herein, and similar in magnitude to spans measured for other PbS₂E_n (E = P or N, *n* = 1 or 2) environments (*i.e.*, **2**, **8** and site 1 of **9**).²⁹ As in the case of **12**, the skew again indicates that δ_{33} is the distinct principal component, which is likely oriented along or near the direction of the Pb lone pair.

³¹P MAS SSNMR spectra were also acquired for **11** (Fig. S2[†]), in the hope of observing indirect spin–spin coupling between ²⁰⁷Pb and neighboring ³¹P nuclei. A single resonance with $\delta_{iso} = 17(1)$ ppm is observed. Since the natural abundance of ²⁰⁷Pb is 22.6%, the coupling is manifested in the form of two satellite peaks, comprising a doublet of *ca.* 22.6% of the total integrated intensity, with ¹J (²⁰⁷Pb, ³¹P) = 1895(100) Hz. This coupling is not visible in the ²⁰⁷Pb CP/CPMG NMR spectrum,

 Table 6
 Experimental ²⁰⁷Pb chemical shift tensor parameters^a

Compound (lead environment)	$\delta_{iso}{}^{c}(ppm)$	$\Omega^d (\mathrm{ppm})$	κ^{e}	δ_{11} (ppm)	$\delta_{22} (\mathrm{ppm})$	$\delta_{33} (\mathrm{ppm})$
$2 (PbS_2N_2)^b$	$2733(5)^{f}$	4700(100)	0.35(7)	4814	3286	114
$7 (PbS_3N)^b$	2873(5)	3900(100)	0.88(10)	4256	4022	356
$8 (PbS_2N)^b$	2852(5)	4500(100)	0.78(15)	4519	4024	19
$12 (PbS_3)$	2750(20)	3400(70)	0.37(5)	4262	3176	812
$11(PbS_2P)$	2610(40)	4400(100)	0.48(5)	4458	3314	58
9 Site 1 (PbS_2N_2)	2706(20)	3600(300)	-0.06(10)	4542	2634	942
9 Site 2 (PbS_3)	3120(20)	3650(200)	0.60(5)	4580	3850	930
10 Site 1 (PbP ₂ S ₂)	-167(50)	1450(100)	0.35(5)	473	2	-977
10 Site 2 (PbS_3)	3040(100)	3580(200)	0.80(5)	4353	3995	773

^{*a*} The principal components of the chemical shift tensor are defined as $\delta_{11} > \delta_{22} > \delta_{33}$, where δ_{11} and δ_{33} are oriented along the directions of lowest and highest shielding, respectively. ^{*b*} CS tensor parameters were previously measured in ref. 29. ^{*c*} $\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$. Values are with respect to neat (CH₃)₄Pb ($\delta_{iso} = 0.0$ ppm). ^{*d*} $\Omega = (\delta_{11} - \delta_{33})$, based upon simulations of static CP/CPMG spectra. ^{*e*} $\kappa = 3(\delta_{22} - \delta_{iso})/\Omega$, $-1.0 < \kappa < +1.0$. ^{*f*} Values in parentheses denote the uncertainty in the last digit of each parameter where indicated.

due to its small magnitude relative to the lead CSA (Ω = 4400 ppm or *ca.* 370 kHz) and the inherently low resolution of the CPMG spectra. It is possible that this coupling might be observed in ²⁰⁷Pb MAS or CP/MAS NMR spectra; unfortunately, these experiments were unsuccessful (refer to ESI[†]) due to lengthy ²⁰⁷Pb T_1 constants and inefficient CP at even very slow spinning rates.

Two distinct but overlapping powder patterns are observed in the 1H-207Pb CP/CPMG and 207Pb WURST-CPMG NMR spectra of compound 9 (Fig. 5), which is consistent with its crystal structure. DFT calculations (vide infra) were used to assign the experimental CS tensors to a crystallographic site. Site 1 of 9 has a four-coordinate PbS₂N₂ environment, with a distorted ψ -trigonal bipyramidal geometry (n.b., the bidentate tmeda ligand binds to Pb in both equatorial and axial positions). Accordingly, this unique lead coordination environment possesses markedly different CS tensor parameters, with Ω = 4050 ppm and κ = 0.07 (though the isotropic shift is still in the same region as those of all of the other sites). The value of Ω observed for site 1 of 9 is slightly less than that previously observed for the analogous complex, 2, which features a similar PbS₂N₂ environment where pyridine ligands bind exclusively in axial positions ($\Omega = 4700 \text{ ppm}$).²⁹ The value of κ for site 1 indicates that all three principal components of the CS tensor are significantly different from one another, making a prediction of the CS tensor orientation based on molecular symmetry alone more difficult. We also note that the poorly resolved low-frequency edge of the spectrum leads to a significant error range in the reported values of the CS tensor element corresponding to the direction of highest magnetic shielding, δ_{33} . Site 2 (distorted ψ -tetrahedral, PbS₃) has Ω = 3600 ppm, similar to the PbS₃ sites of **10** and **12**, and $\kappa = 0.63$, which is intermediate to the κ values of the PbS₃ sites of 10 and 12. δ_{33} is again the distinct component of the CS tensor, and is likely oriented in a similar manner to that described for 10 and 12.

The ¹H-²⁰⁷Pb CP/CPMG and ²⁰⁷Pb WURST-CPMG NMR spectra of **10** show the presence of two well separated and resolved CSA patterns. There are two crystallographically unique Pb sites, sites 1 and 2, which correspond to PbP₂S₂ and

PbS₃ environments, respectively, in a 1:2 ratio. The CS tensor parameters of site 2 (ψ -tetrahedral, PbS₃) are Ω = 3580 ppm and $\kappa = 0.80$, and are similar to the PbS₃ sites of **12** and **9**. As in the cases above, δ_{33} is the distinct component of the CS tensor, and is likely oriented along the pseudo three-fold rotational symmetry axis of the PbS₃ unit. The CS tensor parameters of site 1 (PbP₂S₂) are Ω = 1470 ppm, which is much smaller than those of any of the other systems, and $\kappa = 0.35$, which again indicates that δ_{33} is the distinct component. For site 1, $\delta_{iso} = -167$ ppm, which is much lower than δ_{iso} values observed for all of the other complexes. The disparate CS tensor parameters are most likely observed for site 1 due to the absence of short Pb-S contacts (Pb-S distances of 2.99 Å) and the presence of short Pb–P contacts (Pb–P distances of 2.84 Å). Prediction of the orientation of the CS tensor for site 1 is difficult because of the unique coordination environment of the Pb centre; however, theoretically calculated tensor orientations are discussed below.

Calculation of lead magnetic shielding (MS) tensors with density functional theory

Calculations of NMR parameters using density functional theory (DFT) allow for the correlation of observed NMR parameters to molecular structure, as well as for the exploration of the origins of nuclear magnetic shielding interactions. It is crucial to develop such understandings for unique coordination environments such as the ones described herein, since this will afford rapid structural interpretation for many current and future systems for which crystallographic data is unavailable (i.e., sub-microcrystalline and disordered systems). Furthermore, in compounds containing multiple sites, NMR parameters gleaned from DFT calculations can aid in the assignment of the spectra. In cases where MAS NMR experiments are impractical, these calculations are an invaluable tool for making spectral assignments. Since the current work deals with Pb chemical shifts, the zeroth-order relativistic approximation (ZORA)⁶⁵⁻⁶⁷ was employed for all DFT calculations. This methodology is essential for systems containing heavy atoms, as relativistic effects on the MS tensor become pronounced for heavy nuclei.63,64,76-79

Table 7	Theoretical a	and experimental	MS and CS	tensor parameter
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	$\sigma_{11} (\text{ppm})$	$\sigma_{22} (\mathrm{ppm})$	σ_{33} (ppm)	$\sigma_{\rm iso} ({\rm ppm})$	$\delta_{ m iso}{}^a(m ppm)$	$\Omega(\text{ppm})$	κ
12 (PbS ₂)							
Paramagnetic	-7494	-6071	-5545	-6370		1948	-0.46
Diamagnetic	9956	9959	9964	9960		8	0.27
Spin-orbit	1029	1211	2788	1676		1760	0.79
Total	3785	4931	7082	5266	2799	3297	0.31
Experimental					2750	3400	0.37
11 (PbS ₂ P)							
Paramagnetic	-7969	-5990	-4455	-6138		3514	-0.13
Diamagnetic	9957	9961	9963	9960		6	-0.21
Spin-orbit	1070	1255	3146	1824		2076	0.82
Total	3140	5239	8560	5646	2419	5419	0.23
Experimental					2610	4400	0.48
9 Site 1 (PbS_2N_2)							
Paramagnetic	-8199	-5995	-4126	-6107		4073	-0.08
Diamagnetic	9950	9956	9959	9955		8	-0.32
Spin-orbit	838	1204	3233	1758		2396	0.69
Total	2621	5170	9027	5806	2459	6406	0.20
Experimental					2706	3600	-0.06
9 Site 2 (PbS ₃)							
Paramagnetic	-7050	-6660	-5092	-6267		1958	0.60
Diamagnetic	9956	9961	9962	9960		6	-0.76
Spin–orbit	764	1129	2855	1583		2091	0.65
Total	3816	4452	7556	5275	2790	3740	0.66
Experimental					3120	3650	0.60
10 Site 1 (PbP_2S_2)							
Paramagnetic	-4537	-4400	-3756	-4231		781	0.65
Diamagnetic	9952	9953	9964	9956		12	0.87
Spin–orbit	3013	3172	3322	3169		309	-0.03
Total	8564	8636	9482	8894	-829	919	0.84
Experimental					-167	1450	0.35
10 Site 2 (PbS ₃)							
Paramagnetic	-7825	-6637	-5117	-6527		2708	0.12
Diamagnetic	9957	9961	9964	9960		7	-0.05
Spin-orbit	610	873	2736	1406		2125	0.75
Total	3012	4006	7501	4840	3225	4489	0.56
Experimental					3040	3580	0.80

^{*a*} The principal magnetic shielding tensor components are related to the principal chemical shift tensor components by the equation $\delta_{ii} = \sigma_{ref} - \sigma_{ii}$, where σ_{ref} corresponds to the calculated ²⁰⁷Pb isotropic shielding value of tetramethyllead (PbMe₄, $\sigma_{ref} = 8064.8$). All calculated chemical shift tensor parameters were determined using the formulas provided in Table 6.

The theoretical ²⁰⁷Pb MS tensor parameters for **12** and site 1 of **9** (Table 7) agree well with experimentally determined results, which is gratifying, given the challenging nature of quantum chemical calculations involving heavy atoms such as lead. For the remaining Pb sites, Ω is generally overestimated, except for site 1 of **10** where it is slightly underestimated. Calculated values of κ generally agree well with experimental results, with the exception of **11**. Despite the vast chemical shift range of ²⁰⁷Pb, predicted values of δ_{iso} agree well (*i.e.*, deviate by *ca.* 250 ppm or less) with those observed experimentally, with the exception of site 1 of **10** and, to a lesser extent, site 2 of **9** (conversion of the MS parameters to CS parameters is described in the footnotes of Table 7).

The theoretical lead MS tensor orientations are depicted in Fig. 6. **12** possesses a distorted PbS₃ ψ -tetrahedral coordination environment. As predicted from our experimental data, the MS tensor is oriented such that σ_{33} , the distinct (and most

shielded) principal component, is aligned along the direction of the lone pair, similar to results reported previously.^{29,35} σ_{11} and σ_{22} are directed into unique environments, with σ_{11} aligned near a local pseudo-mirror plane, which explains why the MS tensor is not axially symmetric (*i.e.*, the skew is not close to +1). Compound **11** also contains a single, three coordinate Pb site (PbS₂P), which is in an environment of lower symmetry than that of compound **12**, due to the distinct Pb–P bond which is significantly longer than the Pb–S bonds. In this case, σ_{33} is aligned close to the plane of the two Pb–S bonds (Table 7) in the presumed direction of the electron lone pair.

Two distinct Pb sites are present in **9**: one four-coordinate environment (PbS₂N₂, site 1), and one three-coordinate environment (PbS₃, site 2). Site 2, much like compound **12**, has a distorted ψ -tetrahedral coordination geometry; however, one of the three S atoms has a longer Pb–S bond than the



Fig. 6 Lead MS tensor orientations obtained from ZORA-DFT calculations for complexes 9–12. Angles describing the orientation of principal tensor components with respect to atoms and bond angles are provided in Table S4.1

other two, due to interactions with an adjacent Pb atom. As a result, there is a reduced local symmetry compared to **12**, and σ_{33} is not clearly aligned along a particular symmetry element. The coordination sphere of site 1 of **9** contains two nitrogen atoms and two sulfur atoms, with one of the sulfur atoms positioned between the two distinct Pb sites. σ_{33} is oriented *ca*. 15° from the shorter, covalent Pb–S bond, near the position of the lone pair and σ_{11} is in the same plane as the N–Pb–N bonding arrangement, bisecting the N–Pb–N angle.

Finally, compound 10 has two distinct Pb centres: one fourcoordinate (PbP₂S₂) site (site 1), and two symmetry related, three coordinate (PbS_3) sites (site 2). Site 1 has a unique four coordinate environment, with bonds to a bidentate DMPE ligand, and two long range Pb-S contacts (2.99 Å) to two sulfur atoms from each of the neighboring PbS₃ sites. σ_{33} is aligned in the general direction of the long Pb–S bonds, while σ_{11} and σ_{22} are nearly aligned with the two Pb–P bonds. This tensor orientation indicates that paramagnetic deshielding at the lead center is primarily due to mixing of low-lying virtual Pb-S anti-bonding MOs with high energy occupied Pb-P bonding MOs. For site 2 of 10, one coordinating sulfur atom possesses a long range contact to the adjacent Pb centre of site 1. These lengthened Pb-S bonds reduce the local symmetry at the Pb centre of site 2 of **10**. Accordingly, σ_{33} is shifted away from the pseudo three-fold axis of rotation.

In comparing the Pb MS tensor parameters and orientations, some interesting trends emerge. First, consider the PbS₃ environments in compounds **12**, **9** and **10**. Close examination of the Pb–S bond lengths and S–Pb–S bond angles indicate that **12** is the most symmetric, possessing a local pseudo mirror plane, and **10** is the least symmetric. The orientation of the σ_{33} component of the MS tensor seems to move from the S–Pb–S plane in **9** and **10** and becomes aligned with a pseudo- C_3 axis in **12** as the local symmetry is increased. Clearly, simple symmetry arguments cannot be made to describe these changes in MS tensor parameters and orientations; rather, it is a delicate interplay between paramagnetic shielding contributions involving the Pb lone pair which is a major factor in determining the orientation of these tensors, as we have noted in previous work.²⁹

For the PbS₂P environment of **11** the bond angles are similar to those of the PbS₃ site of **10**; in essence, the difference between the two sites is a phosphorus atom in place of a sulfur atom within the first coordination sphere of the Pb center in **11**. The similar ligand arrangement of the PbS₃ site of **10** and the PbS₂P site of **11** is reflected in the comparability of the calculated MS tensor orientations. However, **11** possesses a much larger Ω and intermediate κ relative to the other three coordinate Pb compounds. The PbP₂S₂ site of **10** is distinct from the PbS₂P site of **11**, due to its higher coordination number and significant lengthening of the Pb–S bonds. Accordingly, the Ω and κ values of the PbP₂S₂ site of **10** are distinct from those of **11**. The reduced span in the PbP₂S₂ site of **10** compared to that in **11** results from a difference in electronic structure at the lead sites (resulting from differing arrangements of the Pb–P bonds, the lengthening of the Pb–S bonds in **10**, *etc.*); notably, the paramagnetic contributions to the CS/MS tensors are greatly reduced in the former (Table 5), consistent with its unique orientation.

Finally, the PbS₂N₂ site of 9, exhibits the second largest Ω in this series of complexes. The PbS₂N₂ environment has an unusual geometry, and undoubtedly has closely spaced occupied and virtual molecular orbitals which are induced to mix by the external magnetic field, thereby giving rise to the large span (a full discussion of this is beyond the scope of the current work). We note that in our previous investigation, the PbS_2N_2 environment of 2 possess a very large Ω value (Ω = 4700 ppm), which we demonstrated was attributable to the presence of a stereochemically active lone pair.²⁹ The value of κ is near zero (the only such case in this series); this is easier to rationalize: each of the CS tensor components are completely different from one another, meaning they arise from mixing of MOs oriented in distinct electronic environments, consistent with the asymmetric nature of this site. Though there are no clear general trends correlating the Ω values and simple structural features, PbS3-type environments tend to have CS tensors which are close to being axially symmetric, whereas the PbS₂P, PbP₂S₂ and PbS₂N₂ sites each have CS tensors with three distinct principal components. Nonetheless, an understanding of the lead CS tensors and orientation dependence and origins in the local lead environments are crucial for future structural interpretation of analogous systems, as well as for developing a fundamental understand of nuclear magnetic shielding of heavy nuclei such as lead.

Conclusions

Coordination complexes incorporating flexible bidentate ligands have been prepared in order to identify new bonding motifs for Pb(II). The reaction of 1 with excess tmeda, dmpe and dppe resulted in isolation of the adducts 9-11, respectively, each of which exhibits a novel bonding environment for Pb(II). Compound 9 shows a dinuclear species in which a tmeda ligand is chelating a distorted *w*-trigonal bipyramidal S_2N_2 Pb(II) center via axial and equatorial sites, while 10 shows a trinuclear species in which the dmpe ligand is chelating the distorted w-trigonal bipyramidal S2P2 Pb(II) center via equatorial sites. Compound 11 shows the dppe ligand bridging two Pb centers, and a distorted *y*-tetrahedral S₂P metal bonding environment. Further, compounds 9 and 10 also exhibit a distorted ψ -tetrahedral (RS)₃Pb arrangement, similar to that previously observed for 12. Compounds 10 and 11 represent the first structurally characterized neutral diphosphine ligand adducts of Pb(II). The observation of both chelating and bridging coordination modes in 9-11 suggests that studies

²⁰⁷Pb SSNMR experiments have been successfully carried out on compounds 9-12. The sensitivity of ²⁰⁷Pb SSNMR as a probe of molecular structure is evident, as the resulting spectra are sensitive to subtle differences in the coordination environment of the Pb centre. The CP/CPMG pulse sequence allows for these spectra to be readily acquired in a piecewise fashion, though employment of the WURST-CPMG sequence allows for each of the spectra to be acquired in a single experiment with comparable total experiment times.⁷⁵ Based on our success with these challenging systems, the WURST-CPMG pulse sequence should be very useful for acquiring wideline SSNMR spectra of spin-half nuclei commonly found in inorganic systems (e.g., ⁷⁷Se, ⁸⁹Y, ¹⁰⁹Ag, ¹¹⁹Sn, ¹²⁵Te, ¹⁸³W, ¹⁹⁵Pt, ¹⁹⁹Hg, ²⁰⁵Tl, ²⁰⁷Pb, etc.), and is necessary for acquiring wideline SSNMR spectra from solids where CP experiments can not be applied (such as oxides and other extended solids devoid of ¹H and ¹⁹F nuclei).

Nuclear magnetic shielding tensors calculated utilizing ZORA-DFT methods agree reasonably well with experimental data, and aid in spectral assignment for cases where multiple Pb sites exist. These calculations also allow for the determination of MS tensor orientations, which correlate spectral parameters to the molecular structure. MS tensor orientations and parameters are highly dependent upon the coordination environment of the Pb centre (i.e., the variation in the number and nature of coordinating ligands). Consequently, we believe that the use of these two pulse sequences for signal enhancement, in combination with DFT calculations of magnetic shielding properties, will allow for many Pb-containing coordination complex materials to be studied using ²⁰⁷Pb SSNMR. We are hopeful that this work inspires further research in this area, and aids others in exploring the nature of lead-containing materials.

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