Translocation-coupled transmetalation at the origin of a dinuclear lead porphyrin complex: implication of a *hanging-atop* coordination mode

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Crystal data for 1_{Pb}.Pb(OAc)

Structural data for 1_{Pb}.Pb(OAc)

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Crystal data for 2^{Pb}

Structural data for 2^{Pb}

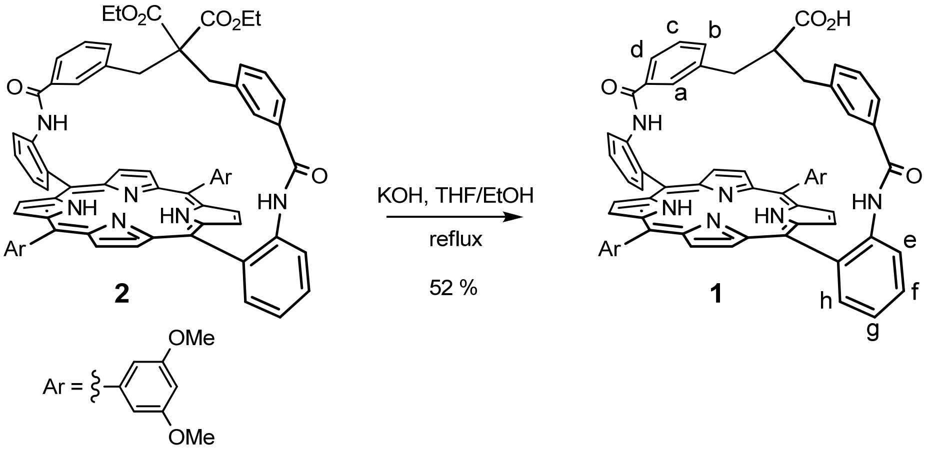
Total energy and cartesian coordinates of the complexes optimized using Gaussian09 at the B88P86/LANL2DZ level of theory (**1_{Pb}.PbOAc**, **1_{Pb}.$PbNO_3$** and **1_{Pb}.PbCl**).

Experimental part

Synthesis of ligand 1.

To a solution of compound **2**[1] (100 mg, 0.086 mmol) in THF (50 mL) was added a solution of KOH (243 mg, 4.0 mmol) in ethanol (10 mL). The reactional mixture was refluxed for two days. At room temperature, an aqueous solution of concentrated HCl (12 M) was slowly added until acidic pH, which led to the precipitation of a green solid. The precipitate was isolated on a glass-filter and washed with water until neutral pH. The solid was dried under vacuum and purified by chromatography (CH_2Cl_2/MeOH 96:4), yielding **1** as a purple solid (48 mg, 52% yield).

^{1}H NMR (DMSO-d_6, 298 K, 500 MHz): δ = 11.81 (1H, s_b, CO_2H), 8.99 (2H, s_b, βpyr), 8.95 (2H, s, NHCO), 8.84 (4H, s_b, βpyr), 8.79 (2H, s_b, βpyr), 8.44 (2H, d, J = 8.2 Hz, He), 8.22 (2H, d, J = 7.4 Hz, Hh), 7.92 (2H, t, J = 7.8 Hz, Hf), 7.72 (3H, m, HAr+Hg), 7.32 (1H, s, HAr), 7.24 (1H, s, HAr), 7.15 (2H, d, J = 7.4 Hz, Hd), 7.13 (1H, s, HAr), 6.89 (4H, m, Hc+HAr), 6.72 (2H, d, J = 7.4 Hz, Hb), 4.84 (2H, s, Ha), 3.93 (3H, s, OMe), 3.91 (3H, s, OMe), 3.85 (3H, s, OMe), 3.83 (3H, s, OMe), 1.97 (1H, m, CHCO), 1.11 (2H, m, CH_{2benz}), 0.86 (2H, m, CH_{2benz}), -2.80 (2H, s, NH_{pyr}). ^{13}C NMR (DMSO-d_6, 298 K, 150 MHz, 15 equiv. DIPEA): δ = 36.6(5), 46.7, 55.3(8), 55.4(0), 55.4(8), 55.6, 100.1, 100.4, 112.8, 113.2,113.6, 144.4, 115.2,119.4, 120.1, 123.1, 124.1, 125.1, 126.1, 128.0, 129.5, 129.8, 134.2, 134.7, 135.2, 138.5, 138.8, 143.0, 143.1, 158.3, 158.6, 158.9, 165.6, 174.5. HRMS (ESI-TOF): m/z calcd for $C_{66}H_{51}N_6O_8$: 1055.3768 $[M-H]^-$; found : 1055.3776. FTIR (KBr): ν = 3640 to 3100, 1684, 1596, 1518, 1449 cm^{-1}. UV-vis (CH_2Cl_2): λ_{max} [nm] (10^{-3} ε [dm^{3}mol^{-1}cm^{-1}]): 424 (363), 516 (16.3), 549 (4.9), 589 (5.7), 645 (2.5).



Scheme S1. Synthesis of ligand **1**.

DFT calculations:

Calculations were carried out at the B88P86/LANL2DZ[2],[3] level of theory using Gaussian09.[4] A full *in vacuo* geometry optimization of **1_{Pb}.PbOAc** was first performed starting from the X-ray experimental structure. The starting structures of **1_{Pb}.$PbNO_3$** and **1_{Pb}.PbCl** were derived from the optimized

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[1] Compound **2** was prepared as previously described: S. Balieu, A. M. Bouraiou, B. Carboni and B. Boitrel, *J. Porphyrins Phthalocyanines,* 2008, **12**, 11-18.

[2] A. D. Becke, *Phys. Rev. A,* 1988, **38**, 3098-3100; (b) J. P. Perdew, *Phys. Rev. B,* 1986, **33**, 8822-8824.

[3] (a) T. H. Dunning Jr. and P. J. Hay, in *Modern Theoretical Chemistry, Vol. 3* (Ed. H. F. Schaefer III), Plenum, New York, 1976, 1-28. (b) W. R. Wadt and P. J. Hay, *J. Chem. Phys.,* 1985, **82**, 284-298.

[4] M. J. Frisch et al. *Gaussian 09*, revision A.02; Gaussian, Inc.: Wallingford, CT, 2009.

geometry of **1_{Pb}.PbOAc** (the AcO$^-$ ligand was discarded and replaced by either a nitrate or a chloride). Optimized structures are shown in Figure S23.

Deformation density isosurfaces (Figure S24) were obtained by substracting from the molecular density of **1_{Pb}.PbOAc**, the self-consistent computed densities of the $[Pb]^{2+}$ and [**1_{Pb}** + DMSO + AcO]$^{2-}$ (for Pb1) or [**1** + DMSO + PbOAc]$^{2-}$ (for Pb2) units, kept with their respective geometries in the dinuclear complex optimized with Gaussian 09. The densities were computed with Amsterdam Density Functional package (ADF2010.2, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com)[5] using Becke's gradient-corrected exchange functional and Perdew's gradient-corrected correlation functional.[2] Triple-ζ quality Slater-type orbital basis sets including polarization functions (TZP) were employed for all atoms to describe valence electrons. Inner shells were kept frozen up to 5d for Pb, 2p for S and 1s for C, N and O, respectively. Scalar relativistic corrections were taken into account within the Zeroth Order Regular Approximation (ZORA).[6]

NMR spectroscopy:

Assignment of the NMR signals of 1, 1^{Pb}, 1_{Pb}.PbOAc

^{1}H and ^{13}C 1D spectra, ^{1}H-^{1}H homonuclear (gdqfCOSY, gROESY) and ^{1}H-^{13}C heteronuclear (gHSQC and 8Hz gHMBC) 2D spectra were recorded at 14.1 T (600 MHz for ^{1}H) and 298 K using a 5 mm shigemi NMR tube. The initial sample was prepared by mixing in the tube 5 mg (4.73 mmol) of **1**, 250 µL of DMSO-d_6 and 7.8 µL of DIPEA (47.2 mmol, 10 equiv.). Samples comprising **1^{Pb}** or **1_{Pb}.PbOAc** as major species were obtained by addition of a suitable amount of $Pb(OAc)_2$. This was completed by successive additions of small volumes of a stock solution prepared by dissolving 18 mg (47.4 mmol) of $Pb(OAc)_2$ in 100 µL of DMSO-d_6 (5 µL = 0.5 equiv.). Similarly, a sample of **1^{Pb}** formed upon addition of one equiv. of $PbCl_2$ was used for signals assignment. Selected spectra are shown in Figures S4-S13 and S18-S21. For proton labelling, see Figure S15.

1^{Pb}: ^{1}H NMR (DMSO-d_6, 298 K, 600 MHz): δ = 9.20 (2H, s, CONH), 8.96 (2H, d, J = 4.8 Hz, Hp), 8.92 (2H, d, J = 4.8 Hz, Hm/n), 8.89 (2H, d, J = 4.2 Hz, Hn/m), 8.82 (4H, m, Ho+e), 8.12 (2H, d, J = 7.2 Hz, Hh), 7.88 (2H, t, J = 8.1 Hz, Hf), 7.71 (1H, s_b, Hj), 7.64 (2H, t, J = 7.2 Hz, Hg), 7.33 (1H, s_b, Hi/i'), 7.26 (2H, d, J = 7.8 Hz, Hd), 7.23 (1H, s_b, Hi'/i), 7.09 (1H, s_b, Hj'), 6.94 (4H, m, Hc+k/l), 6.82 (2H, d, J = 7.2 Hz, Hb), 5.08 (2H, s, Ha), 3.90 (6H, s, OMe), 3.85 (3H, s, OMe), 3.80 (3H, s, OMe), 1.55 (2H, m, CH_2out), 1.10 (1H, m, CHCO), 0.90 (2H, m, CH_2in).

1_{Pb}.PbOAc: ^{1}H NMR (DMSO-d_6, 298 K, 600 MHz): δ = 9.20 (2H, d, J = 3.6 Hz, Hp), 9.11 (2H, d, J = 4.2 Hz, Ho), 9.04 (2H, d_b, J = 5.4 Hz, He), 8.84 (2H, d, J = 4.2 Hz, Hm), 8.70 (2H, d, J = 3.6 Hz, Hn), 8.29 (2H, d_b, J = 6.0 Hz, Hh), 7.95 (1H, s_b, Hj), 7.87 (2H, t, J = 7.8 Hz, Hf), 7.70 (1H, s_b, Hi'/i), 7.64 (2H, t, J = 7.5 Hz, Hg), 7.40 (1H, s_b, Hj'), 7.16 (2H, d, J = 7.2 Hz, Hd), 6.99 (1H, s, Hk/l), 6.95 (2H, t, J = 7.5 Hz, Hc), 6.89 (2H, s_b, Hk/l+i'/i), 6.82 (2H, d, J = 7.2 Hz, Hb), 5.48 (2H, s, Ha), 4.00 (3H, s, OMe), 3.98 (3H, s,OMe), 3.91 (3H, s, OMe), 3.68 (3H, s, OMe), 2.35 (2H, m, CH_2out), 1.85 (2H, m, CH_2in), 1.05 (1H, m, CHCO), 0.27 (3H, s_b, CH_3CO).

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[5] (a) C. Fonseca Guerra, J. G. Snijders, G. te Velde and E. J. Baerends, *Theo. Chem. Acc.,* 1998, **99**, 391-403; (b) G. te Velde, F. M. Bickelhaupt, C. Fonseca Guerra, S. J. A. van Gisbergen, E. J. Baerends, J. G. Snijders and T. Ziegler, *J. Comput. Chem.,* 2001, **22**, 931-967.

[6] (a) E. van Lenthe, E. J. Baerends and J. G. Snijders, *J. Chem. Phys.,* 1993, **99**, 4597-4610; (b) E. van Lenthe, E. J. Baerends and J. G. Snijders, *J. Chem. Phys.,* 1994, **101**, 9783-9792; (c) E. van Lenthe, R. van Leeuwen, E. J. Baerends and J. G. Snijders, *Int. J. Quantum Chem.,* 1996, **57**, 281-293.

^{1}H NMR titration of 1 with Pb(OAc)$_2$ and determination of the association constants

The initial sample was prepared in a 5 mm standard NMR tube by mixing 3 mg (2.84 mmol) of **1**, 600 µL of DMSO-d_6 and 4.7 µL of DIPEA (28.4 mmol, 10 equiv.); the concentration of **1** was 4.69 × 10^{-3} mol/L. A ^{1}H spectrum of this initial sample was recorded. Aliquots of the stock solution of Pb(OAc)$_2$ prepared in DMSO-d_6 (6 µL ≈ 0.25 equiv.) were then added and at least one ^{1}H spectrum was recorded after each addition of Pb(OAc)$_2$. Successive spectra recorded for the same sample were identical, indicating that equilibrium is reached instantaneously.
The ^{1}H 1D NMR spectra were recorded at 14.1 T (600 MHz for ^{1}H) and 298 K using a 5 mm inverse-detection probe and the following acquisition parameters: relaxation delay of 17 s, high-power RF pulse of 6.7 µs (about 90°), acquisition time of 3 s and 16 transients (scans). The spectral width was about 20 ppm, centered at 4 ppm. The processing comprised exponential multiplication of the free induction decay (line broadening factor lb = 0.3 Hz), zero-filling, Fourier transform, phase corrections, chemical shift calibration (residual CHD$_2$ signal of the solvent set to 2.50 ppm) and base line correction. The spectra are shown in Figures S14 and S15.

The simplest model describing the binding of lead in the presence of acetate ions corresponds the following generic equilibriums:

$$\mathbf{1} + \mathrm{Pb}^{2+} \rightleftharpoons \mathbf{1}^{\mathbf{Pb}} \tag{1}$$

$$\mathbf{1}^{\mathbf{Pb}} + \mathrm{Pb}^{2+} \xrightleftharpoons{\text{acetate}} \mathbf{1_{Pb}.PbOAc} \tag{2}$$

In both these equations Pb^{2+} stands for lead ions free in solution. Despite the notation used for the bimetallic complex (**$\mathbf{1_{Pb}}$.PbOAc**), the binding of the anion AcO^- is not explicitly considered in equation (2). The corresponding equilibrium constants, Ka_1 (L/mol) and Ka_2' (L/mol), must therefore be considered as apparent association constants. They can be written as:

$$Ka_1 = \frac{1}{C_\mathbf{1}} \frac{v}{u\,(R - v - 2w)} \tag{3}$$

$$Ka_2' = \frac{1}{C_\mathbf{1}} \frac{w}{v\,(R - v - 2w)} \tag{4}$$

where $C_\mathbf{1}$ is the total molar concentration of **1** (it is not constant as a consequence of dilution).

R is the number of equivalents of Pb(II) : $R = C_{Pb}/C_\mathbf{1}$, with C_{Pb} standing for the analytical molar concentration of Pb(II).

u, v and w are, respectively, the mole fraction of free **1**, mononuclear complex $\mathbf{1^{Pb}}$ and dinuclear complex **$\mathbf{1_{Pb}}$.PbOAc** at equilibrium : $u=[\mathbf{1}]/C_\mathbf{1}$; $v=[\mathbf{1^{Pb}}]/C_\mathbf{1}$; $w=[\mathbf{1_{Pb}.PbOAc}]/C_\mathbf{1}$

In these equations, (R - v - 2w) corresponds to the number of equivalents of free Pb(II) in solution, *i.e.* $[Pb]/C_\mathbf{1}$. Using equation (5), equations (3) and (4) can be transformed into equations (6) and (7), respectively.

$$w = 1 - u - v \tag{5}$$

$$u^2 + \frac{R - 2 + v}{2} u - \frac{v}{2Ka_1 C_\mathbf{1}} = 0 \tag{6}$$

$$v^2 + \left(R - 2 + 2u + \frac{1}{Ka_2' C_\mathbf{1}} \right) v - \frac{1 - u}{Ka_2' C_\mathbf{1}} = 0 \tag{7}$$

Obviously, for R = 0 the solutions of these equations are u = 1, v = 0 and w = 0. Equations (6) and (7) were solved iteratively for increasing values of R (34 values ranging between 10^{-4} and 3.5, among which the experimental values), starting by equation (7). The initial value of u was computed as:

$$u(R+dR) = u(R) + \frac{\partial u}{\partial R}(R) \times dR + \frac{1}{2}\frac{\partial^2 u}{\partial R^2}(R) \times dR^2 \qquad (8)$$

Analytic expressions for the first and second derivatives were obtained from equations (6) and (7). Convergence, defined as a variation in u and in v smaller than 10^{-5}, was achieved in less than 20 iterations.

The kinetics of the lead binding processes are slow on the NMR spectral time scale and, therefore, signal integration can be used to determine the mole fractions u, v and w. Integration of the signal(s) of acetate was used to determine the actual value of the ratio R. Integrals were determined by deconvolution of the spectral regions of interest using Lorentzian functions for the NMR signals and appropriate functions for the local baseline (Figures S2 and S3). The digital resolution of the spectra used for this purpose was 0.73 Hz/pt. The mole fractions u, v and w were determined using (i) the signals of Ha (2H, observed between 4.8 and 5.5 ppm) and (ii) the signals of Hh (2H, observed between 8.1 and 8.3 ppm). The ratio R was obtained using the total integral of the signals of free and bound acetate (3H, observed at about 1.8 ppm and 0.27 ppm, respectively) and the average value of total integral determined for Ha and Hh.

The best fit of equations (5-7) to the average value of the u, v and w experimental data determined using the signals of Ha and Hh are shown in Figure S1a. The agreement is excellent. The apparent association constants (adjustable parameters) are Ka_1= 2.5 × 10^4 L/mol and Ka_2' = 1.6 × 10^3 L/mol.

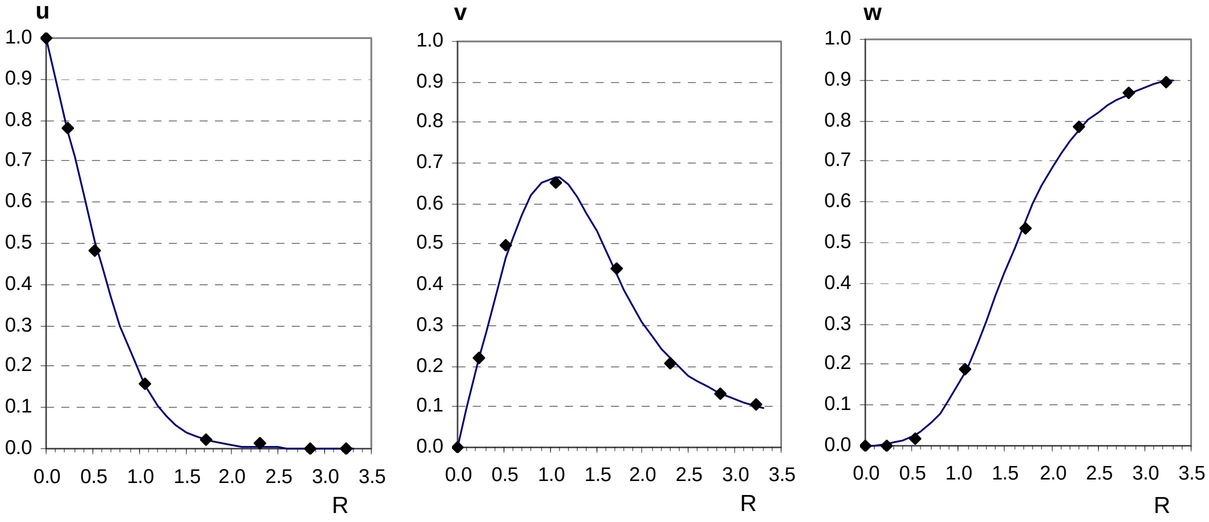


Figure S1a. Analysis of the ^{1}H NMR titration of **1** with $Pb(OAc)_2$ according to equilibriums (1) and (2). u: mole fraction of free **1**; v: mole fraction of mononuclear complex $\mathbf{1^{Pb}}$; w: mole fraction of dinuclear complex $\mathbf{1_{Pb}.PbOAc}$. The lines are the results of the best fit of equations (5-7) to the experimental data (♦).

As mentioned above, the binding of the anion AcO^- is not explicitly considered in equation (2). This is legitimate for a large (and constant) excess of acetate ions but, in view of the protocol of the titration experiment, the validity of such an approximation is questionable. A priori, the formation of the bimetallic complex should be better described by the following equilibrium:

$$\mathbf{1^{Pb}} + \mathrm{Pb^{2+}} + \mathrm{Acetate} \rightleftharpoons \mathbf{1_{Pb}.PbOAc} \qquad (9)$$

where Acetate stands for AcO$^-$ free in solution. The corresponding equilibrium constant, Ka$_2$ (L^2/mol^2) can be written as:

$$\mathrm{Ka}_2 = \frac{1}{C_1}\frac{w}{v\,(R-v-2w)} \times \frac{1}{C_1}\frac{1}{(2R-w)} \qquad (10)$$

where (2R - w) corresponds to the number of equivalents of free acetate in solution, *i.e.* [Acetate]/C$_1$.

The use of equation (5) would yield a cubic polynomial in the variable v, which is not handy for solving. Equation (10) can be written in a form similar to equation (7) but with Ka$_2$(2R-w)C$_1^2$ instead of Ka$_2$'C$_1$:

$$v^2 + \left(R - 2 + 2u + \frac{1}{\mathrm{Ka}_2(2R-w)C_1^{\,2}}\right)v - \frac{1-u}{\mathrm{Ka}_2(2R-w)C_1^{\,2}} = 0 \qquad (11)$$

Equation (11) was also solved iteratively with u constant and w computed via equation (5). Convergence, defined as a variation in v smaller than 10^{-5}, was achieved in less than 5 iterations.

The best fit of equations (5-6) and (11) to the average value of the u, v and w experimental data are shown in Figure S1b. The overall agreement is very good but some discrepancy is observed at the largest R values. This could be due to the fact that Pb(OAc)$_2$ is less dissociated as its concentration increases and, consequently, the model overestimates the amount of acetate ions free in solution. The analysis yields Ka$_1$= 1.3 × 10^4 L/mol and Ka$_2$= 9.3 × 10^4 L^2/mol^2. As might have been expected, both models yield similar values for the apparent association constant characterizing the formation of the monometallic complex.

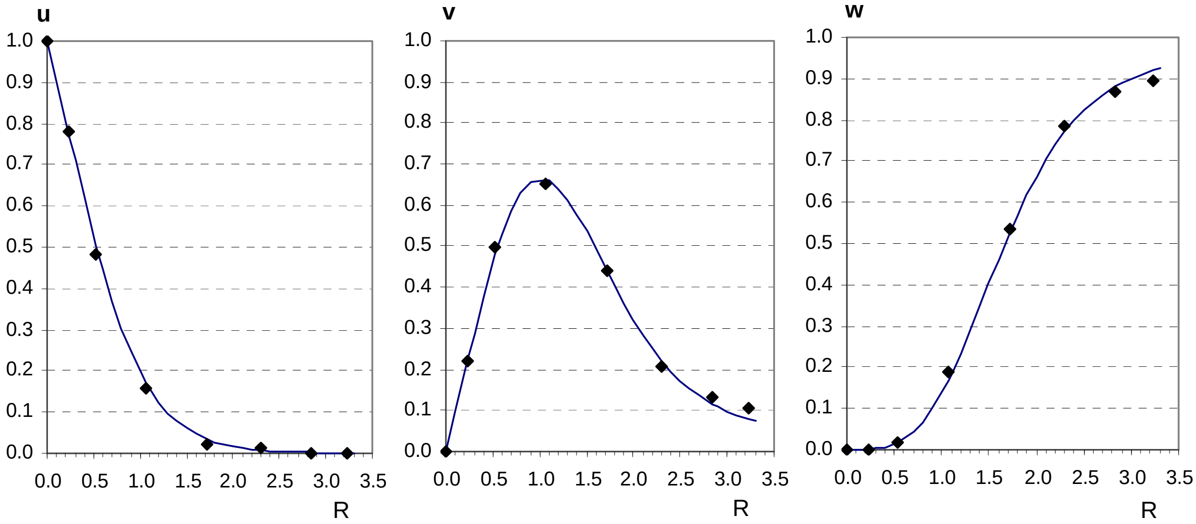


Figure S1b. Analysis of the ^{1}H NMR titration of **1** with Pb(OAc)$_2$ according to equilibriums (1) and (9). u: mole fraction of free **1**; v: mole fraction of mononuclear complex $\mathbf{1^{Pb}}$; w: mole fraction of dinuclear complex $\mathbf{1_{Pb}.PbOAc}$. The lines are the results of the best fit of equations (5-6) and (11) to the experimental data (♦).

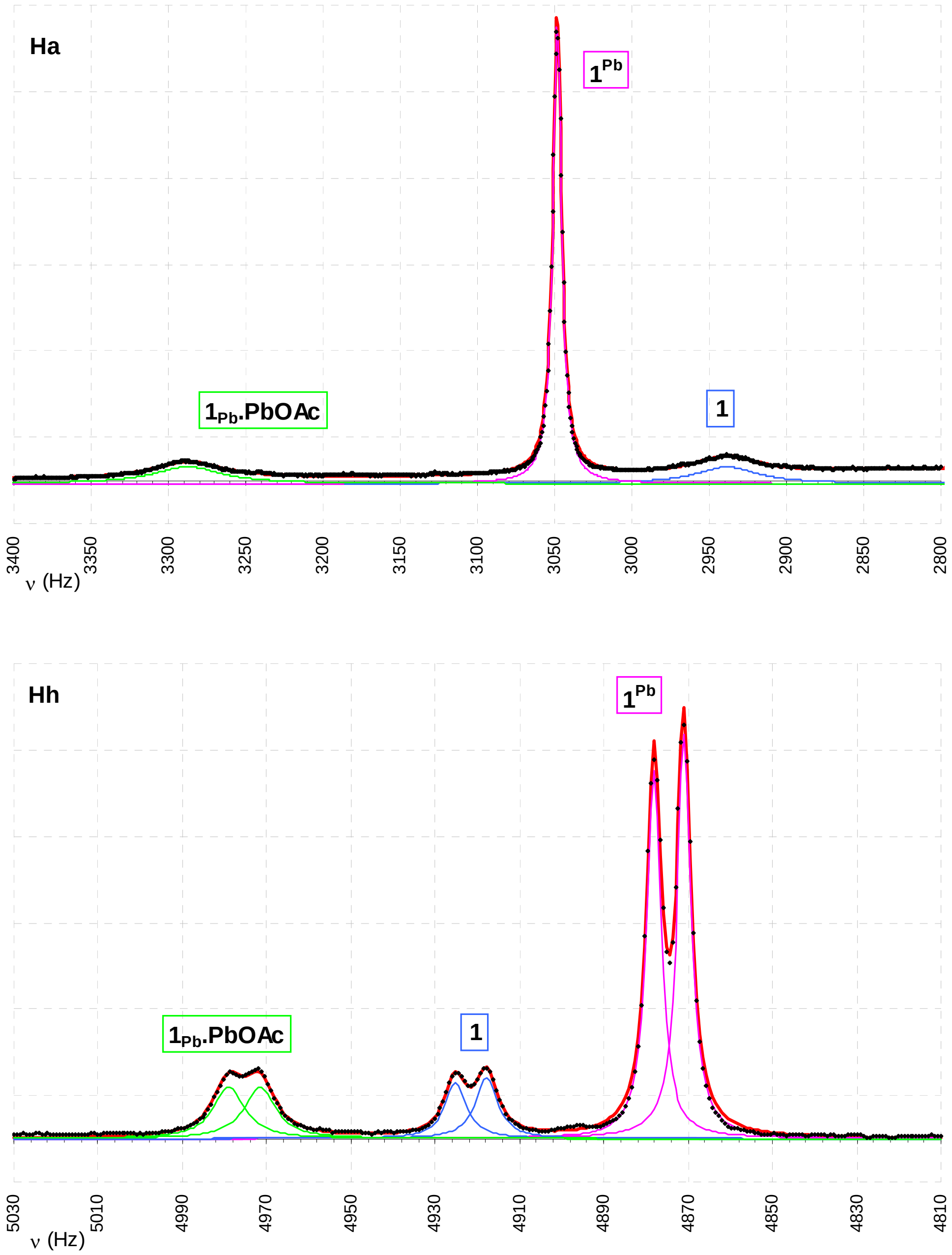


Figure S2. ^{1}H NMR titration of **1** with Pb(OAc)$_2$: deconvolution of the regions of the ^{1}H NMR spectrum (1 ppm = 600 Hz) recorded for R ≈ 1 showing the singlet Ha signals (above, fitted local baseline not shown) and the doublet Hh signals (below ; for the three signals, the scalar coupling constant was constrained to be identical; for each doublet signal, the linewidth of the two components was constrained to be identical). The experimental data points are in black and the deconvoluted spectra in red.

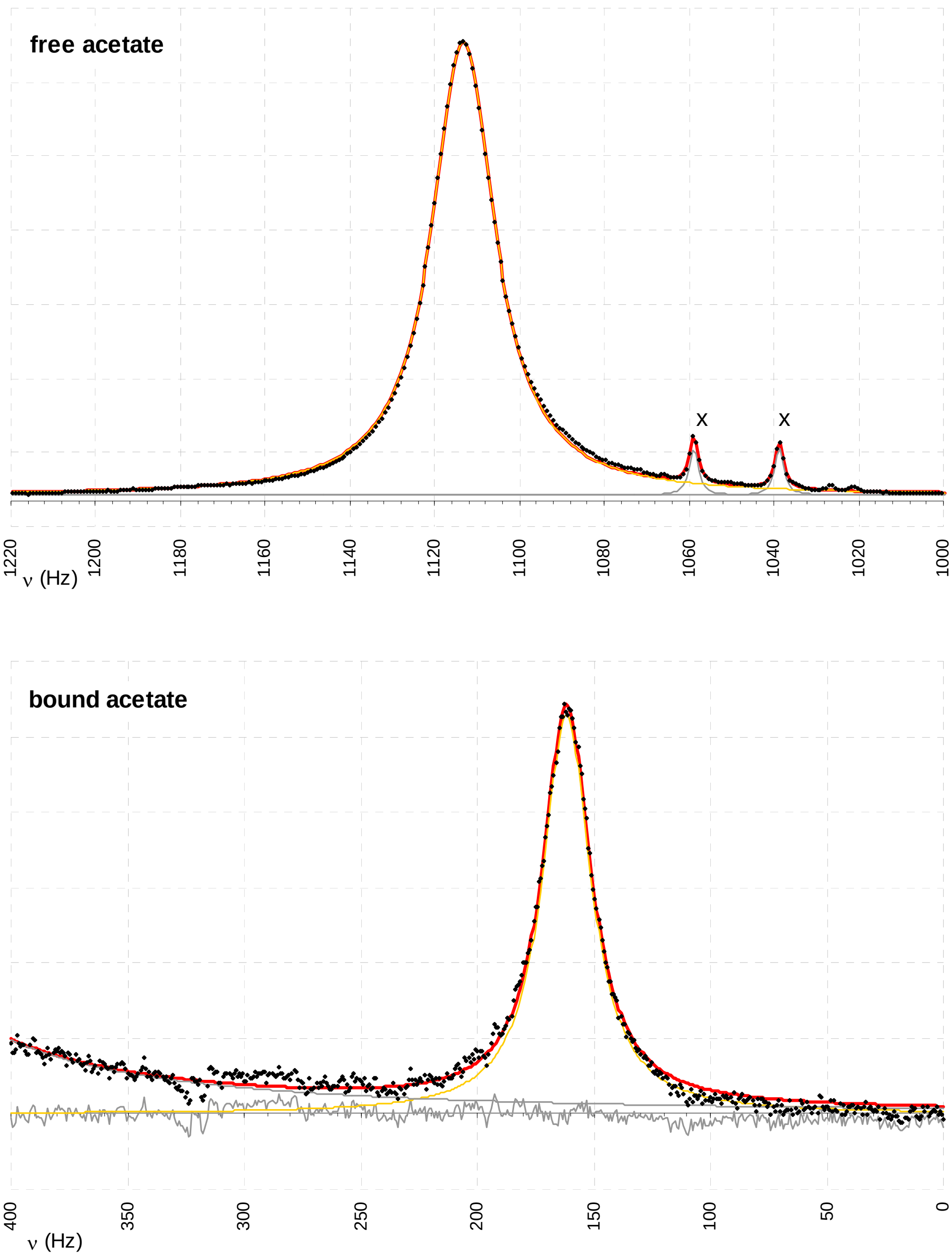
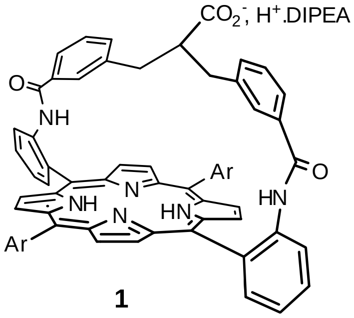


Figure S3. ^{1}H NMR titration of **1** with Pb(OAc)$_2$: deconvolution of the regions of the ^{1}H NMR spectrum (1 ppm = 600 Hz) recorded for R ≈ 1 showing the singlet signals of free and bound acetate. The experimental data points are in black and the deconvoluted spectra in red. The signals of acetate are in orange and the baseline in grey (X = impurity signal). The difference between the experimental and deconvoluted spectra is shown for the region of bound acetate.



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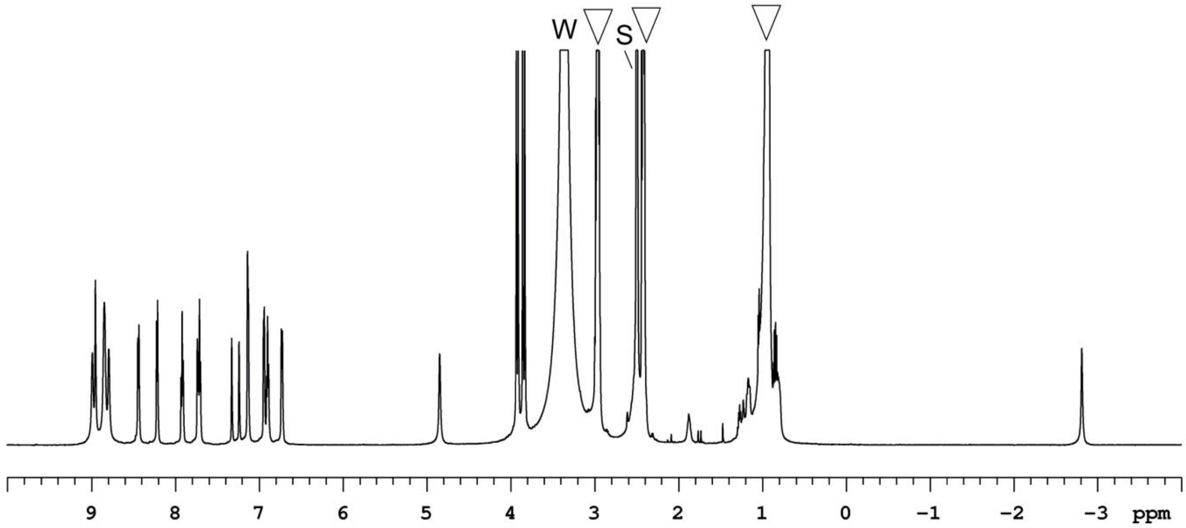
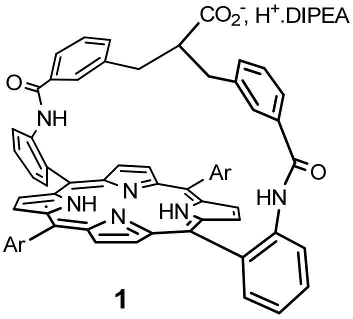


Figure S4. ^{1}H NMR spectrum of **1** (DMSO-d_6, 600 MHz, 10 equiv. DIPEA [▼]). S = solvent; W = water.



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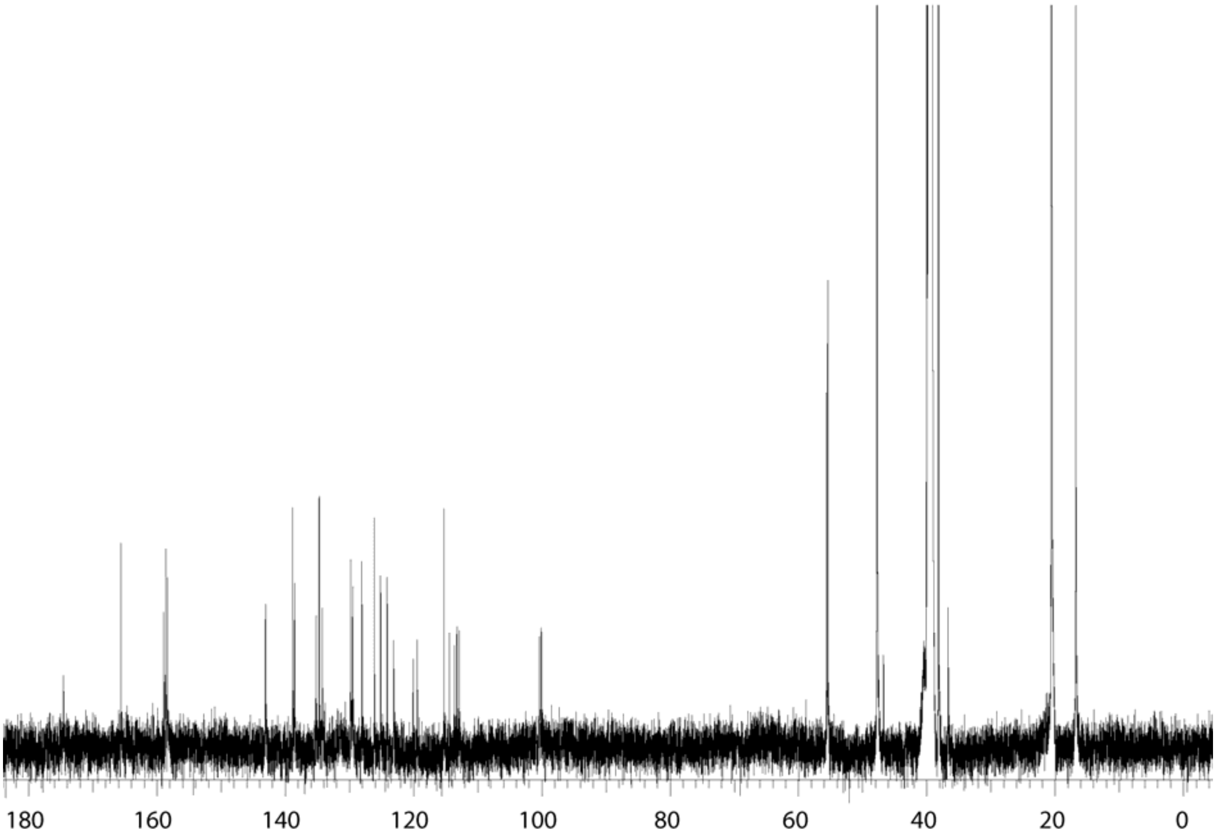
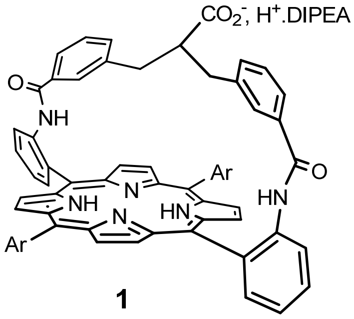


Figure S5. ^{13}C NMR spectrum of **1** (DMSO-d_6, 150 MHz, 10 equiv. DIPEA).



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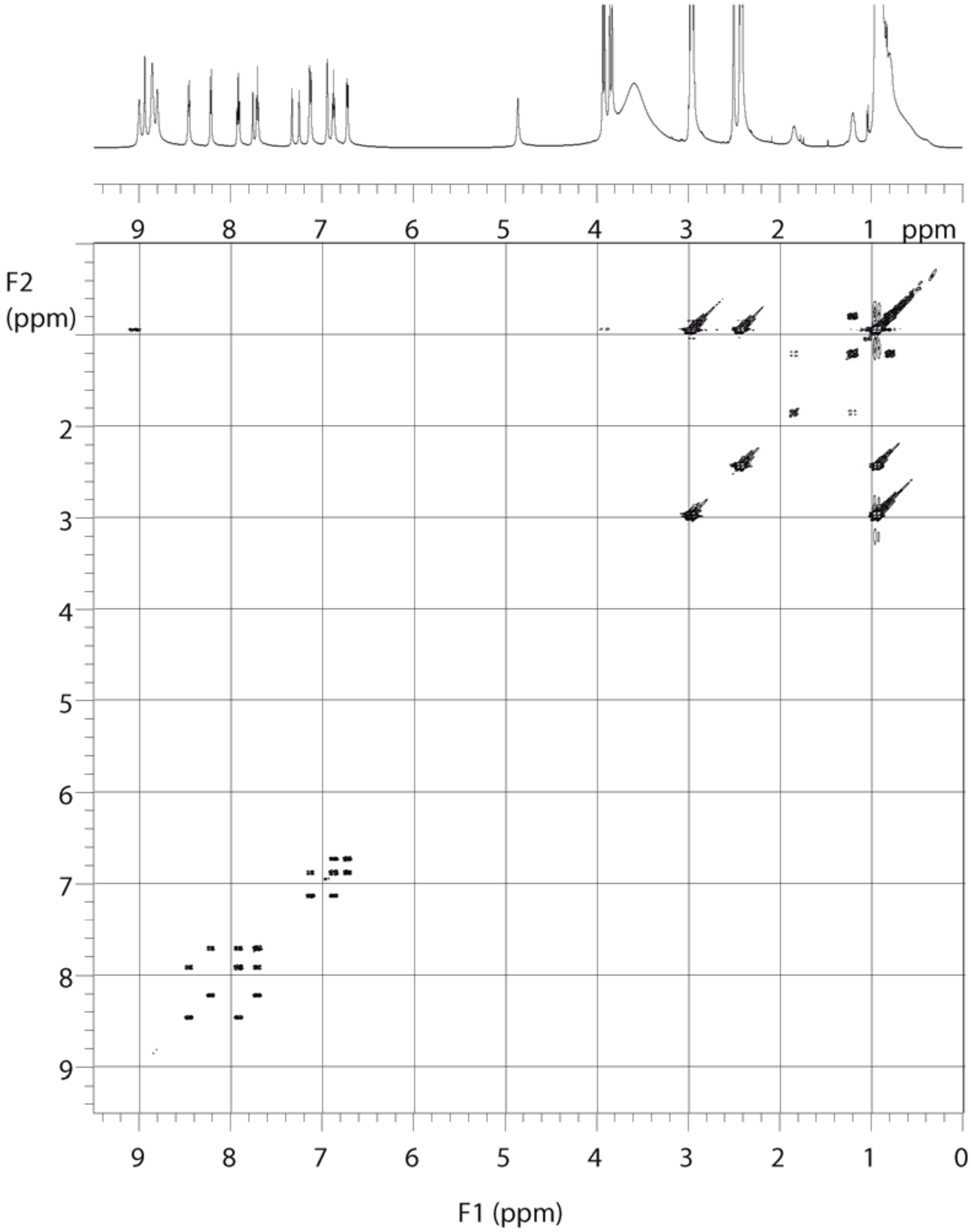
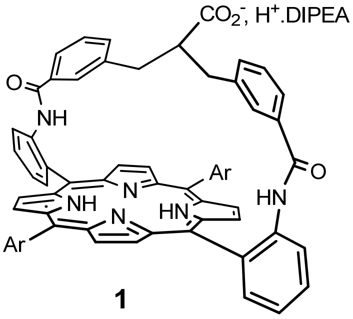


Figure S6. COSY 2D NMR spectrum of **1** (DMSO-d_6, 600 MHz, 10 equiv. DIPEA).



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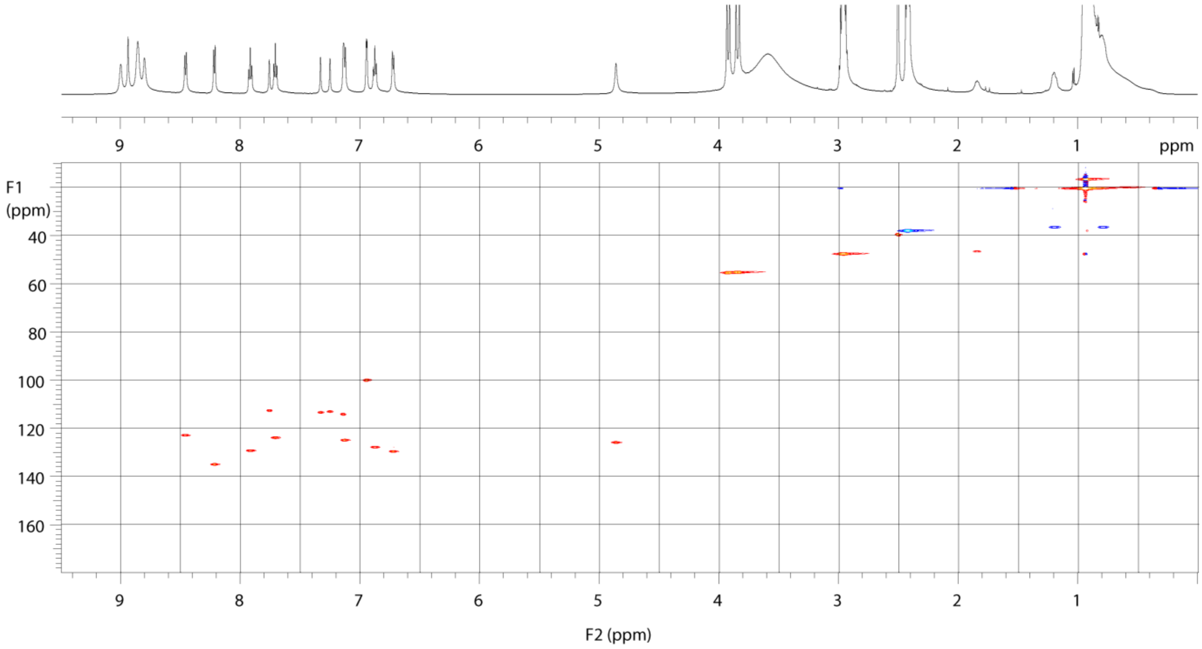
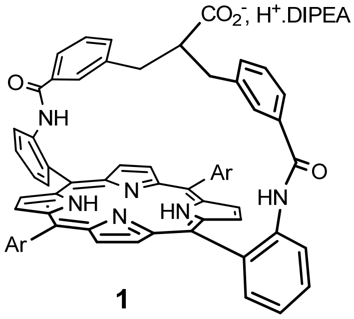


Figure S7. HSQC 2D NMR spectrum of **1** (DMSO-d_6, 600 MHz, 10 equiv. DIPEA).



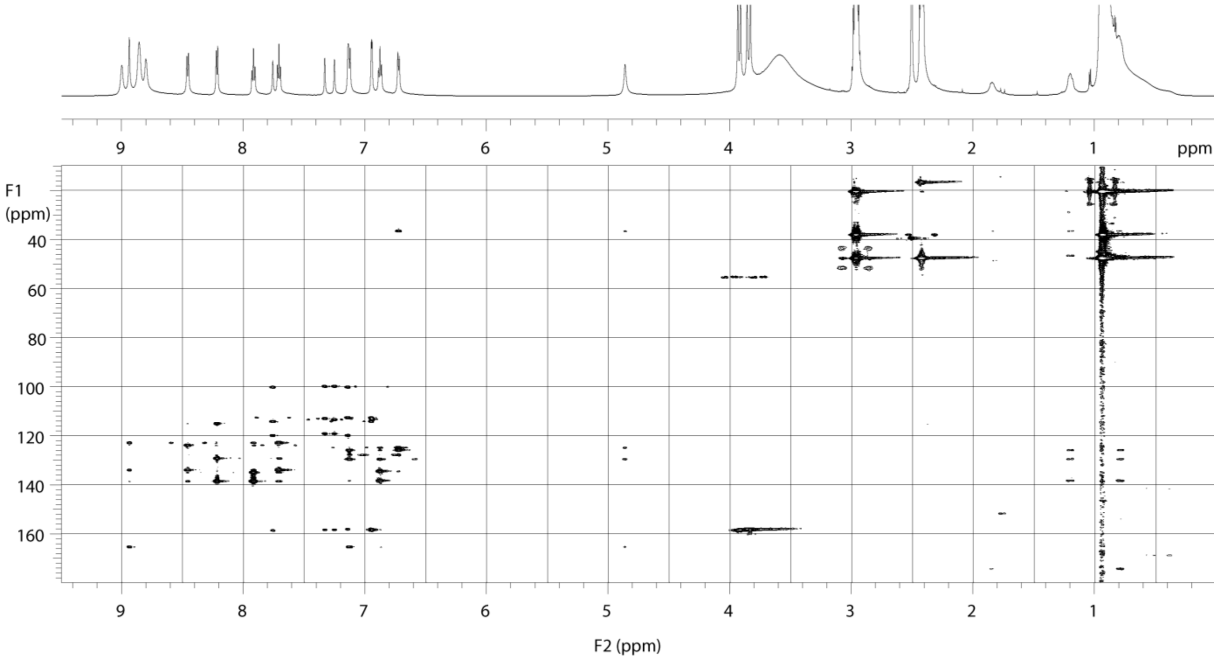
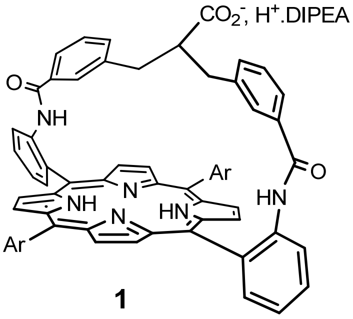


Figure S8. HMBC 2D NMR spectrum of **1** (DMSO-d_6, 600 MHz, 10 equiv. DIPEA).



1

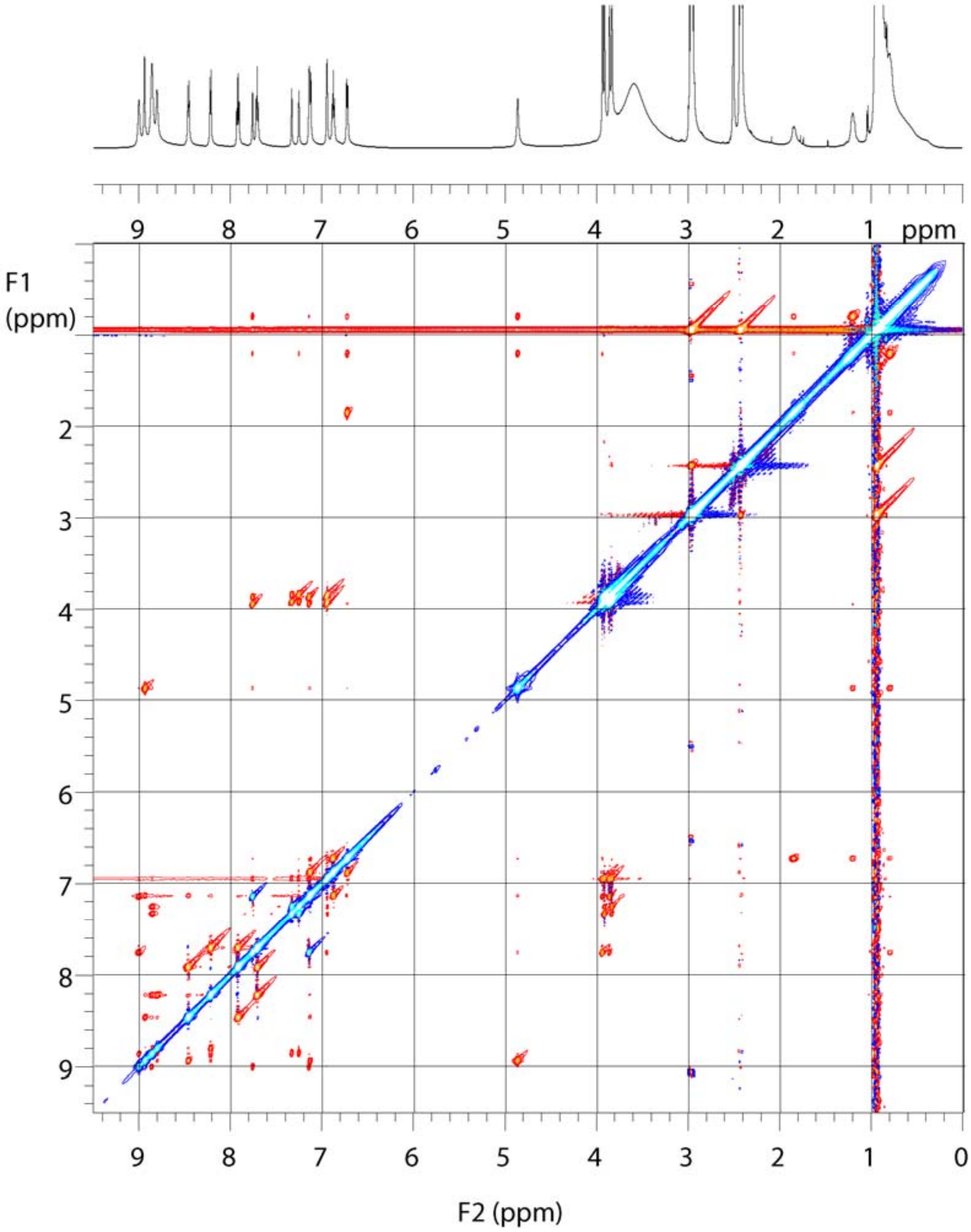
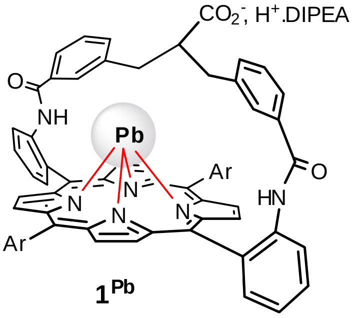


Figure S9. ROESY 2D NMR spectrum of **1** (DMSO-d_6, 600 MHz, 10 equiv. DIPEA).



1^{Pb}

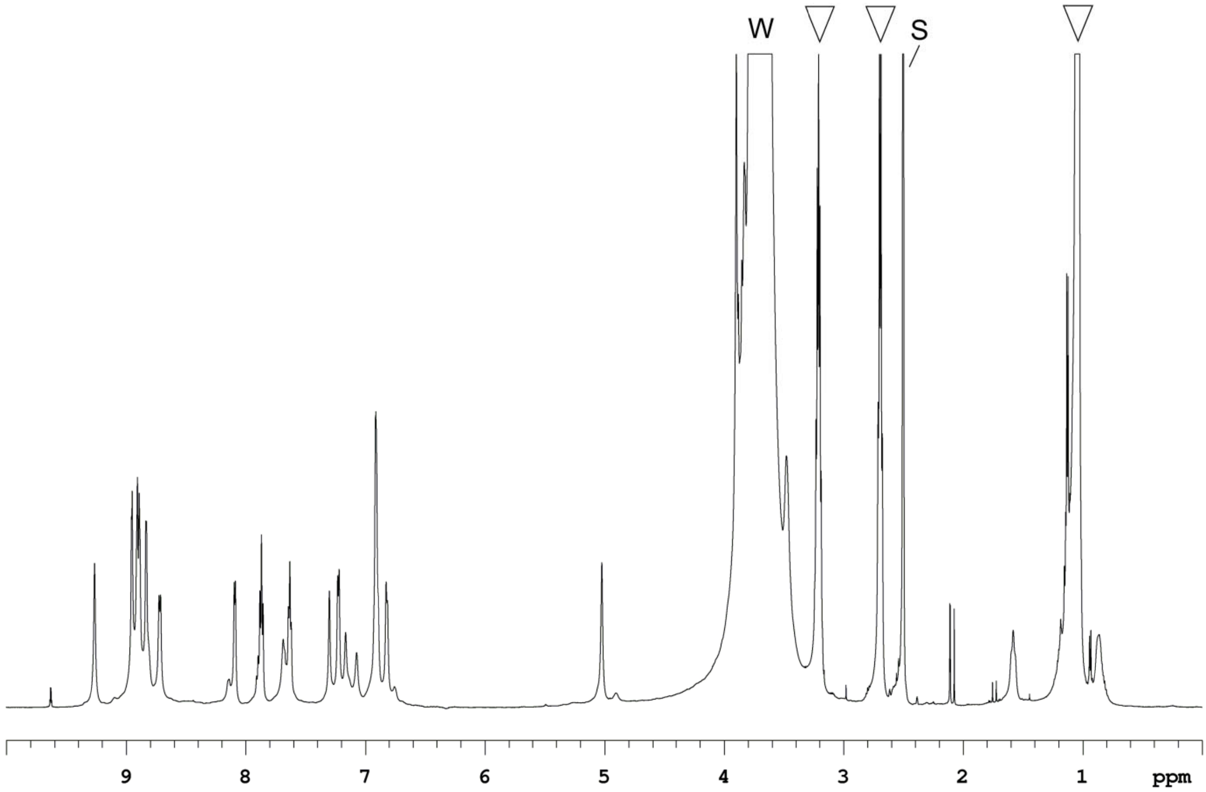
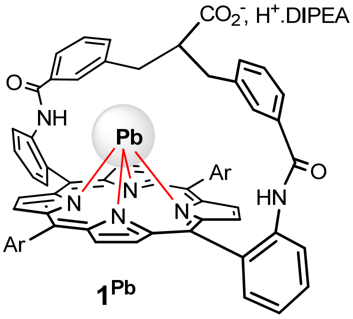


Figure S10. ^{1}H NMR spectrum of **1^{Pb}** (DMSO-d_6, 600 MHz, 10 equiv. DIPEA [▽]), formed upon addition of one equiv. of $PbCl_2$ to **1**. S = solvent; W = water.



1^{Pb}

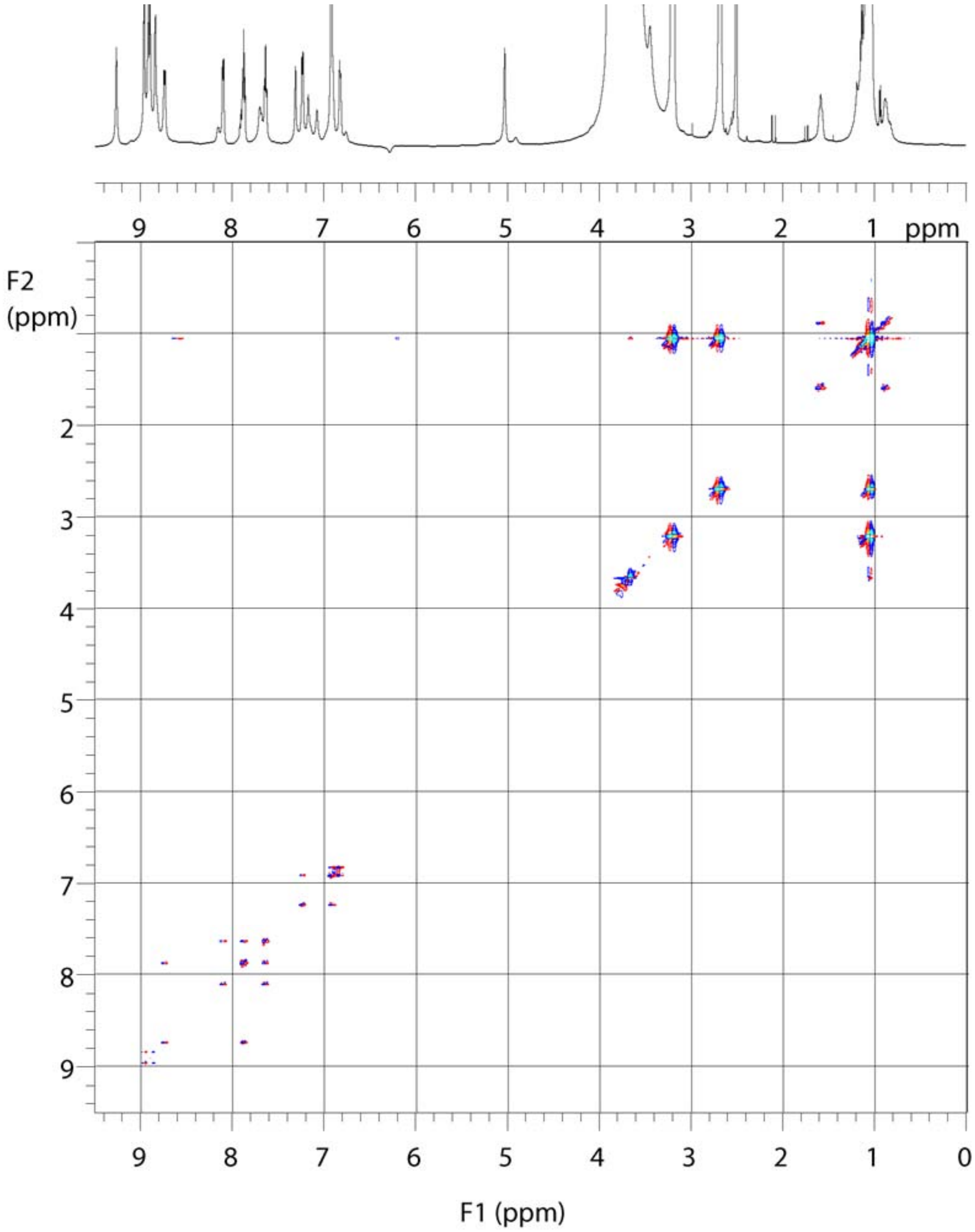
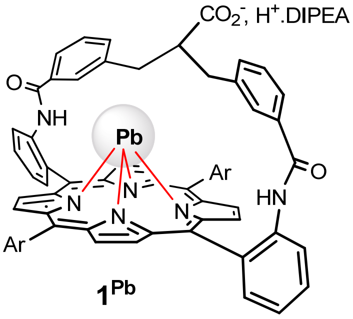


Figure S11. 2D COSY NMR spectrum of **1**^{Pb} (DMSO-d_6, 600 MHz, 10 equiv. DIPEA), formed upon addition of one equiv. of $PbCl_2$ to **1**.



1^{Pb}

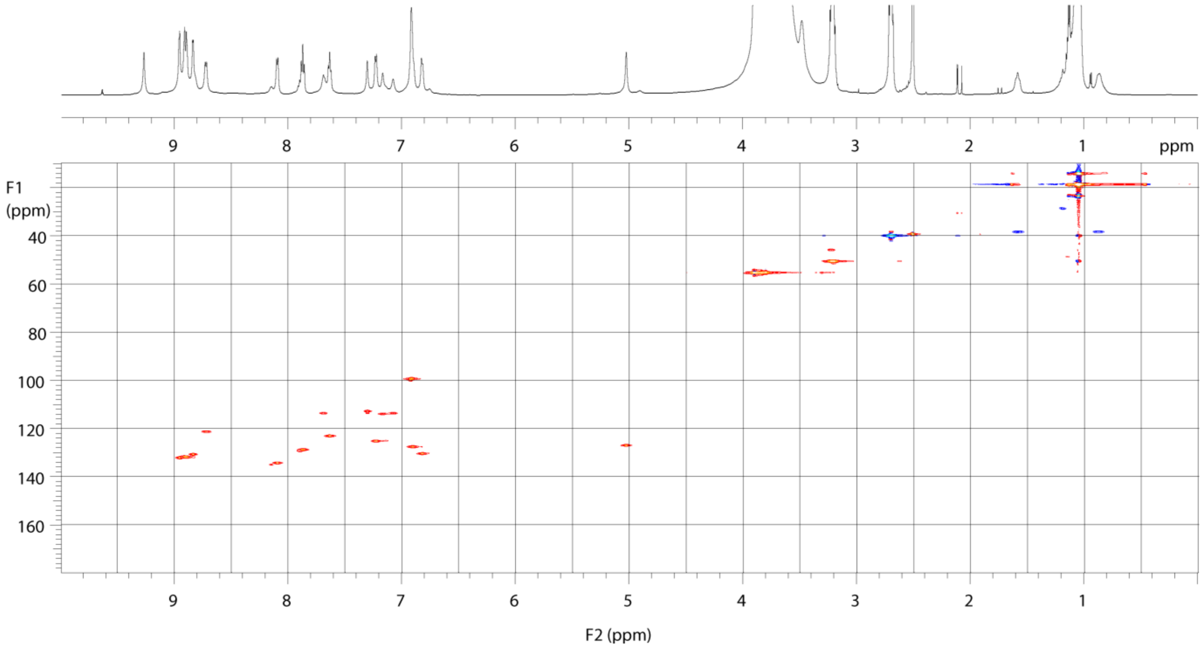
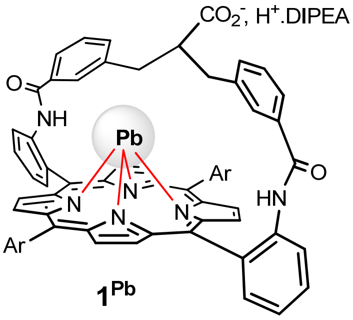


Figure S12. 2D HSQC NMR spectrum of $\mathbf{1}^{\mathbf{Pb}}$ (DMSO-d_6, 600 MHz, 10 equiv. DIPEA), formed upon addition of one equiv. of $PbCl_2$ to **1**.



1^{Pb}

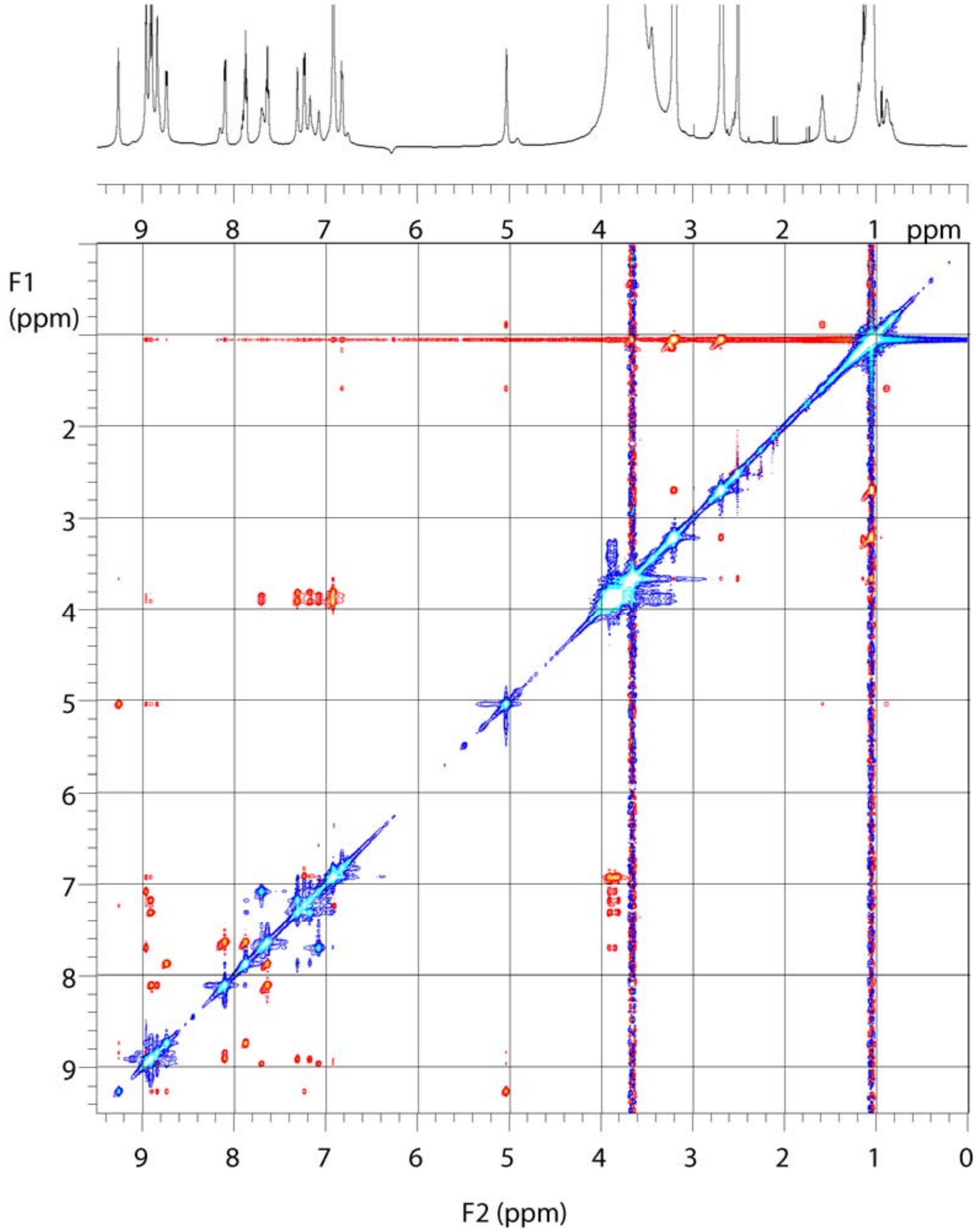


Figure S13. 2D ROESY NMR spectrum of **1**^{Pb} (DMSO-d_6, 600 MHz, 10 equiv. DIPEA), formed upon addition of one equiv. of PbCl$_2$ to **1**.

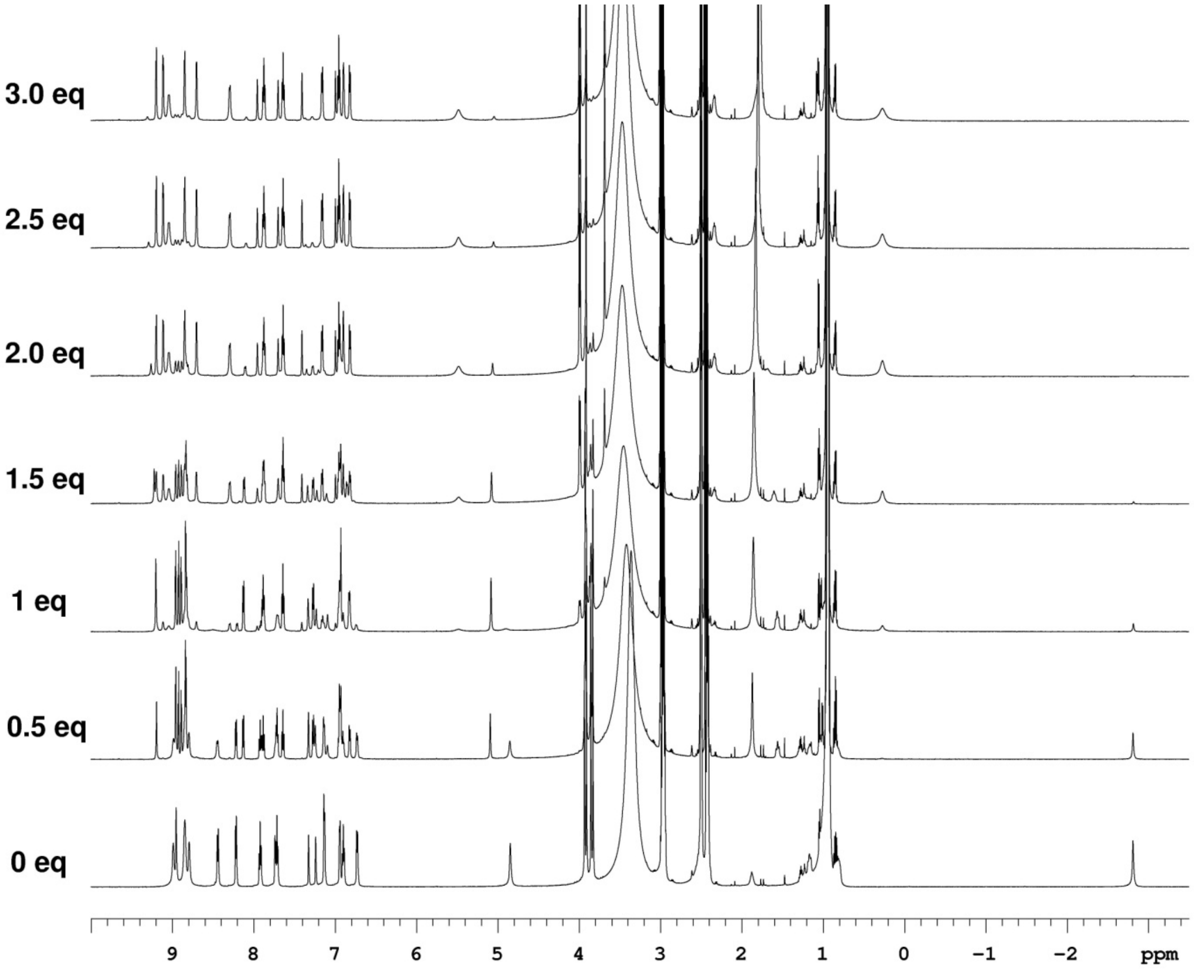


Figure S14. ^{1}H NMR spectra (DMSO-d_6, 600 MHz, 10 equiv. DIPEA) for the complexation of lead(II) by ligand **1:** titration with Pb(OAc)$_2$.

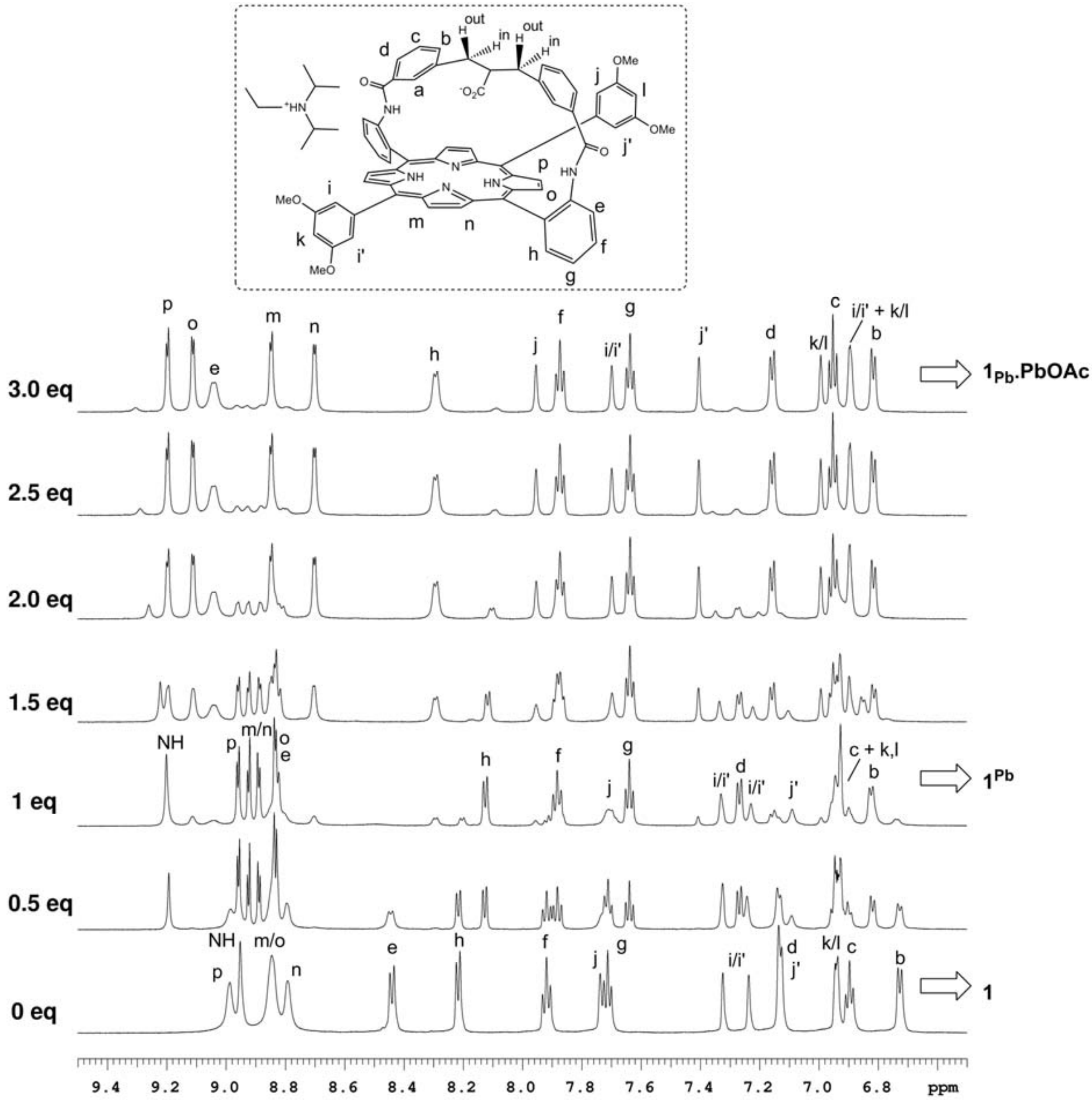


Figure S15. ^{1}H NMR spectra (DMSO-d_6, 600 MHz, 10 equiv. DIPEA) for the complexation of lead(II) by ligand **1:** titration with $Pb(OAc)_2$. Expanded view and full attribution of the aromatic part of the spectra.

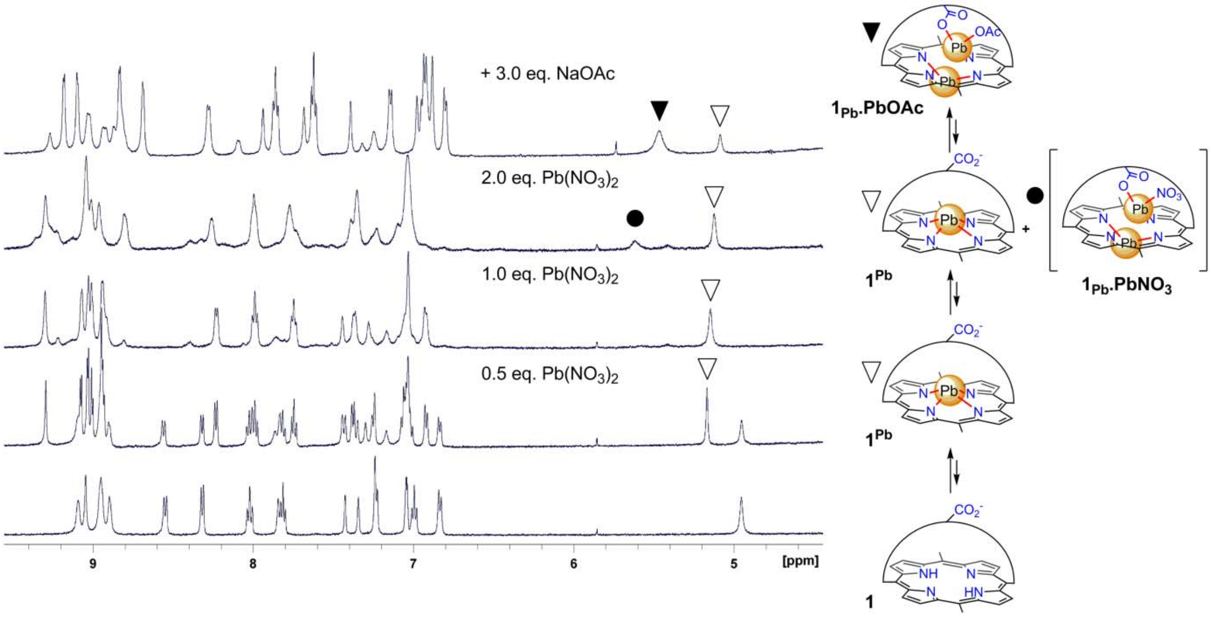


Figure S16. ^{1}H NMR spectra (DMSO-d_6, 500 MHz, 15 equiv. DIPEA) for the complexation of lead(II) by ligand **1:** titration with Pb(NO$_3$)$_2$, and subsequent addition of NaOAc; expanded view on the aromatic part of the spectra.

Additionnal comment: with excess of Pb(NO$_3$)$_2$, a minor species is observed together with **1^{Pb}** (black circle). According to DFT studies (see text), this species could correspond to a dinuclear complex, namely **1_{Pb}.PbNO$_3$**, similar to the one formed with Pb(OAc)$_2$.

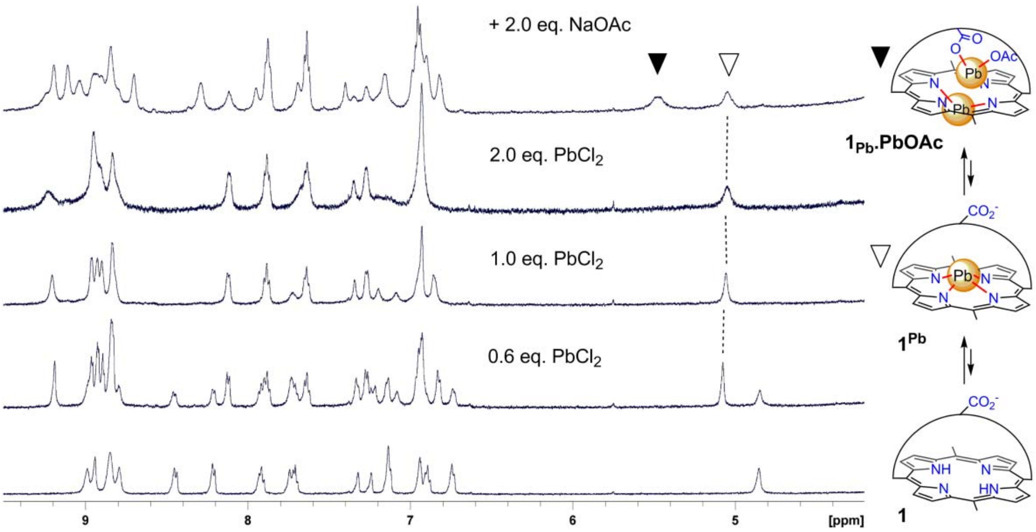


Figure S17. ^{1}H NMR spectra (DMSO-d_6, 500 MHz, 15 equiv. DIPEA) for the complexation of lead(II) by ligand **1:** titration with $PbCl_2$, and subsequent addition of NaOAc; expanded view on the aromatic part of the spectra.

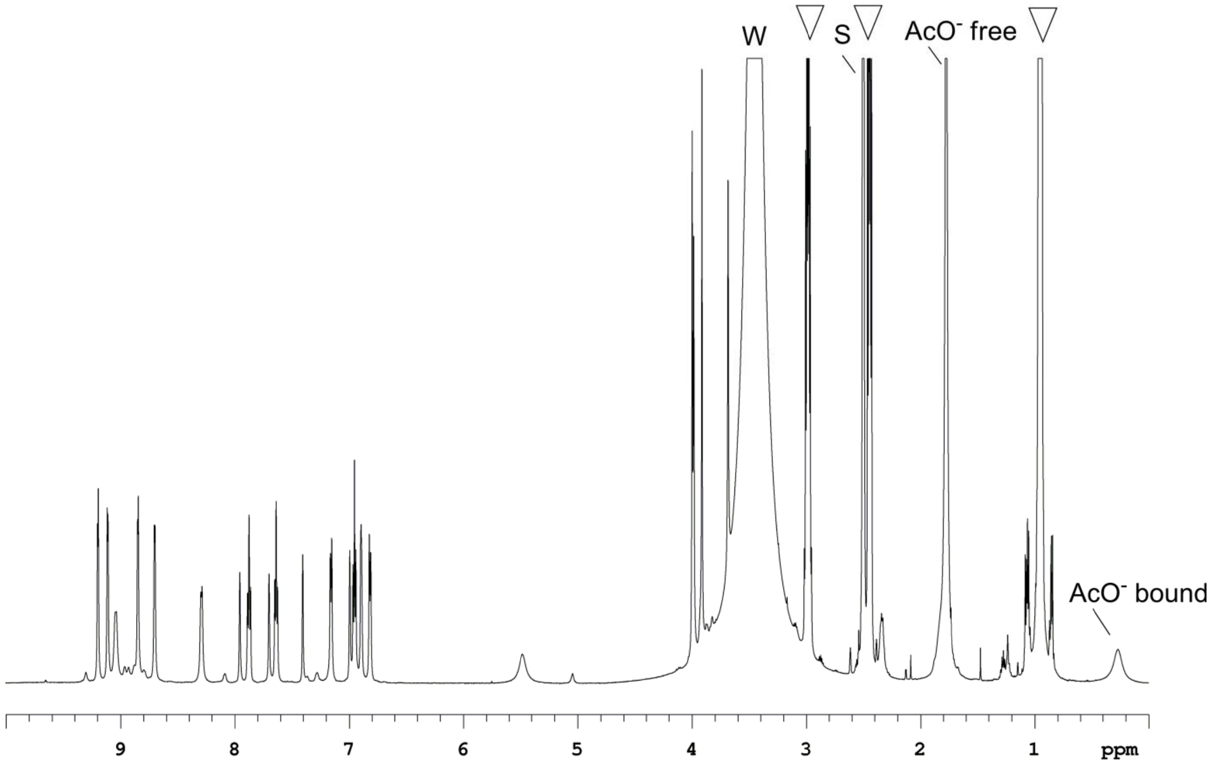
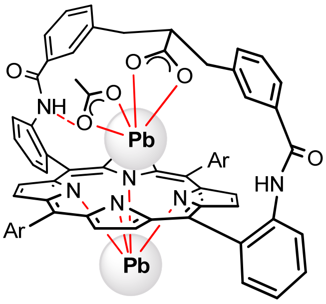


Figure S18. ^{1}H NMR spectrum of $\mathbf{1_{Pb}.PbOAc}$ (DMSO-d_6, 600 MHz, 10 equiv. DIPEA [▽]), formed upon addition of three equiv. of $Pb(OAc)_2$ to **1**. S = solvent; W = water.



1_{Pb}.PbOAc

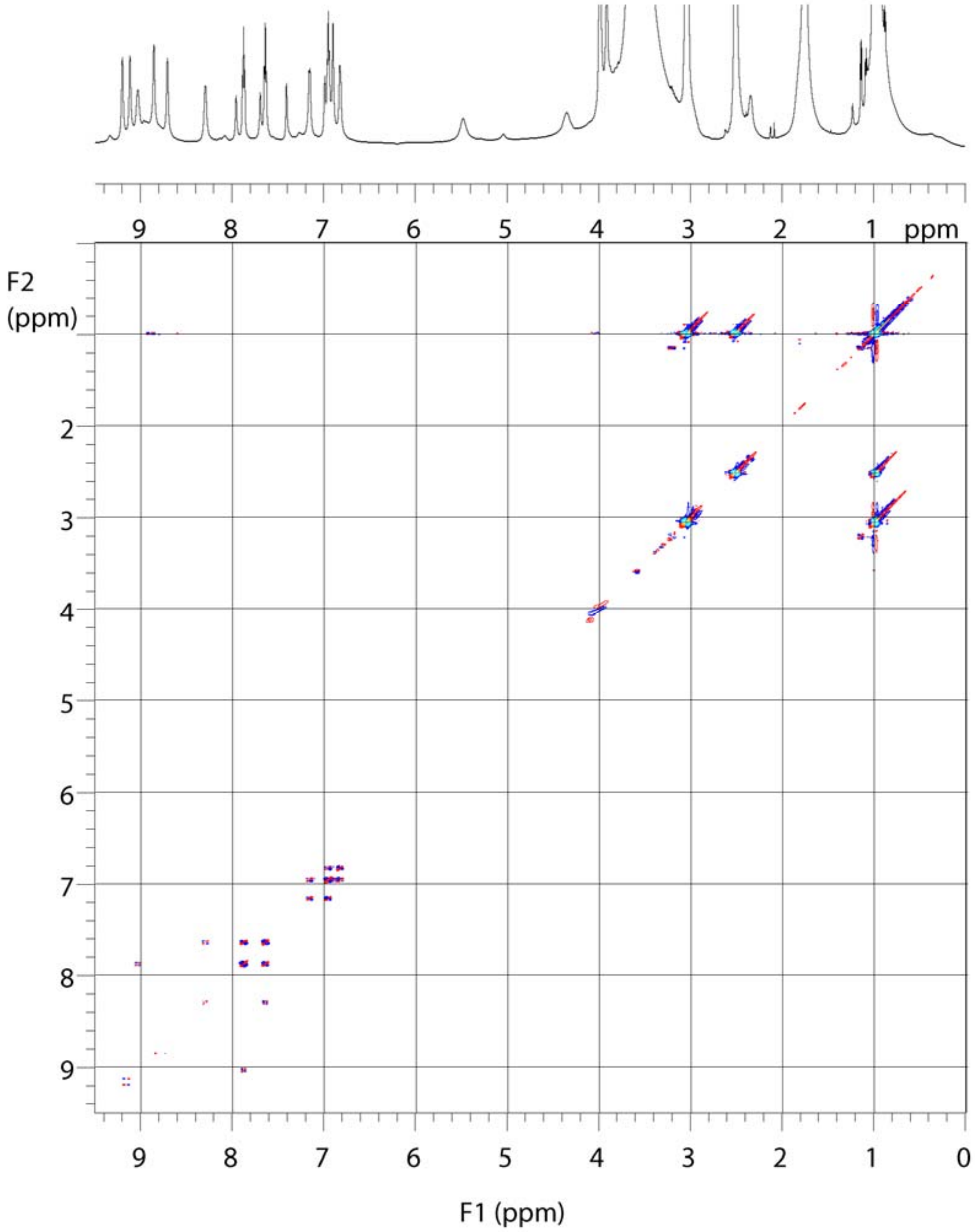
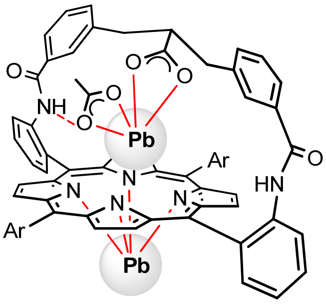


Figure S19. 2D COSY NMR spectrum of **1_{Pb}.PbOAc** (DMSO-d_6, 600 MHz, 10 equiv. DIPEA), formed upon addition of 2.5 equiv. of $Pb(OAc)_2$ to **1**.



1$_{Pb}$.PbOAc

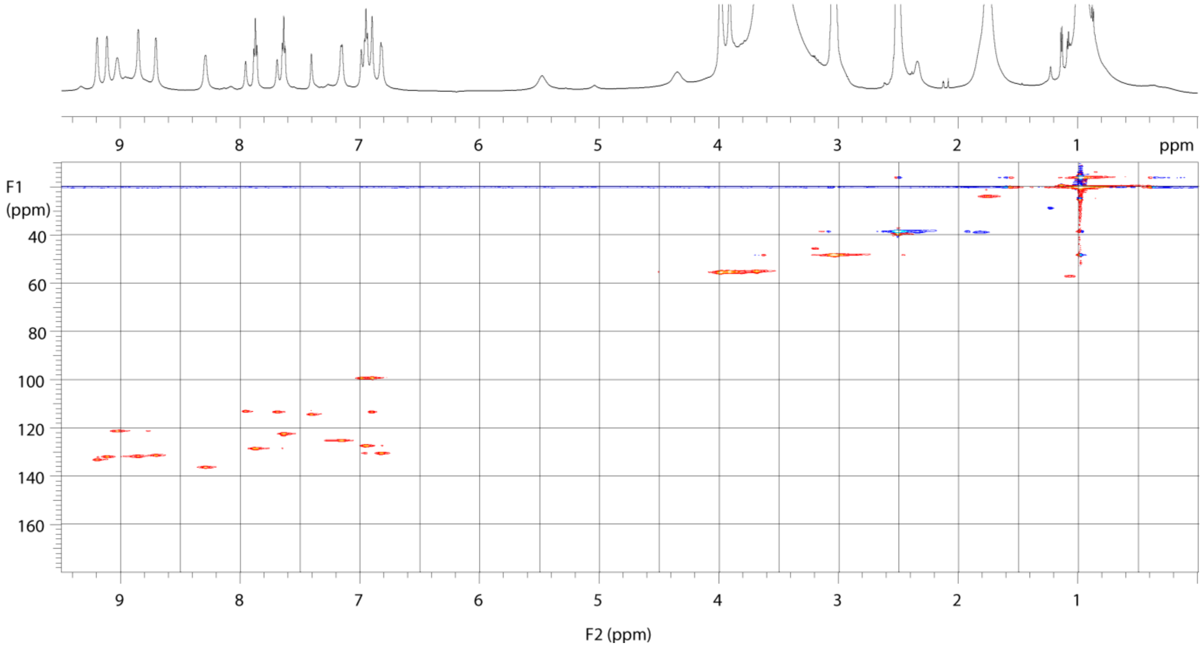
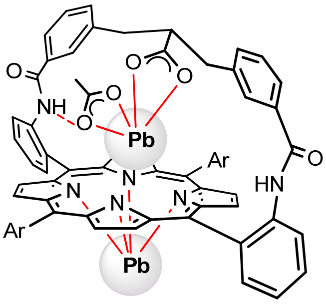


Figure S20. 2D HSQC NMR spectrum of **1$_{Pb}$.PbOAc** (DMSO-d_6, 600 MHz, 10 equiv. DIPEA), formed upon addition of 2.5 equiv. of Pb(OAc)$_2$ to **1**.



$\mathbf{1_{Pb}}$.PbOAc

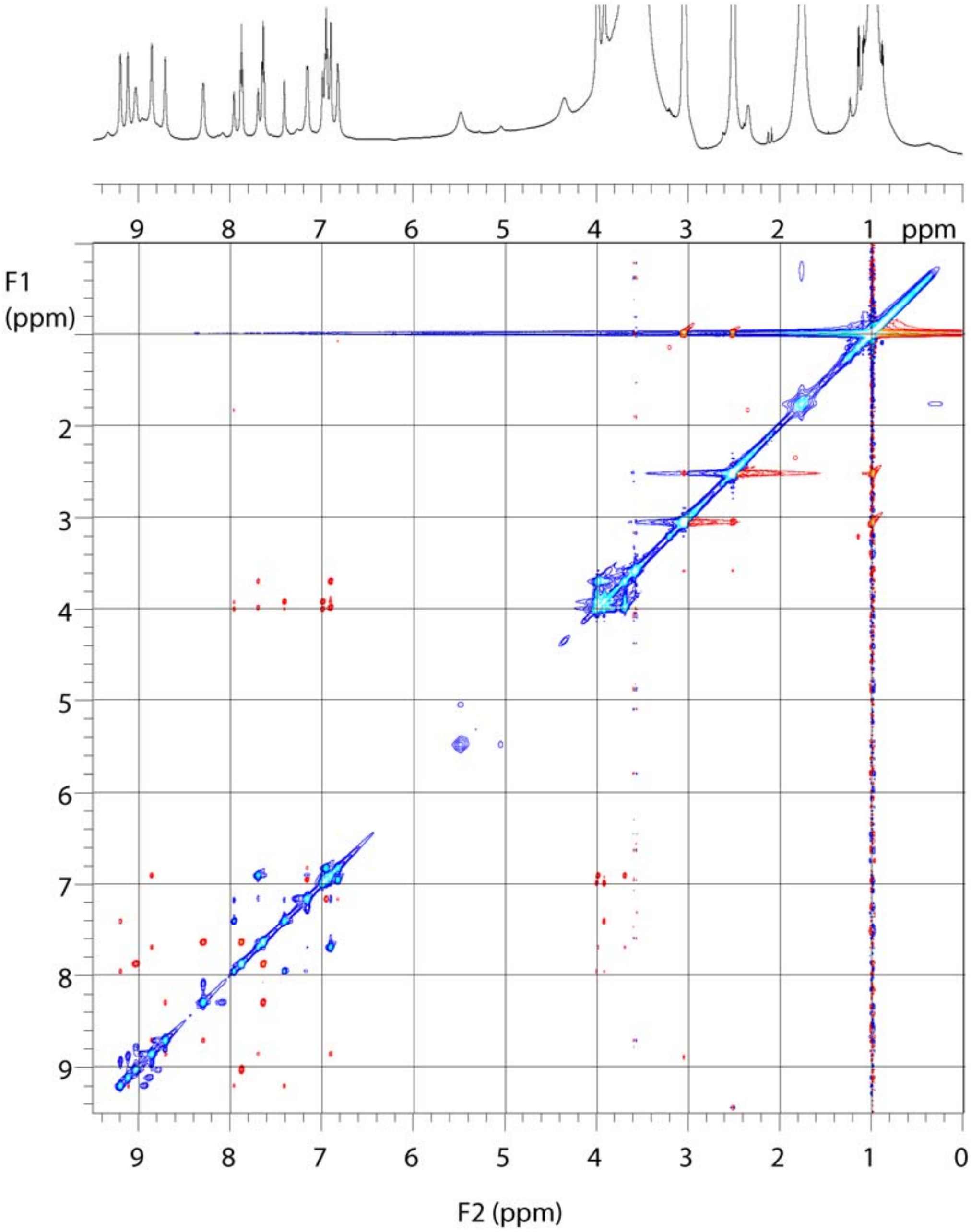


Figure S21. 2D ROESY NMR spectrum of **1_{Pb}.PbOAc** (DMSO-d_6, 600 MHz, 10 equiv. DIPEA), formed upon addition of 2.5 equiv. of Pb(OAc)$_2$ to **1**.

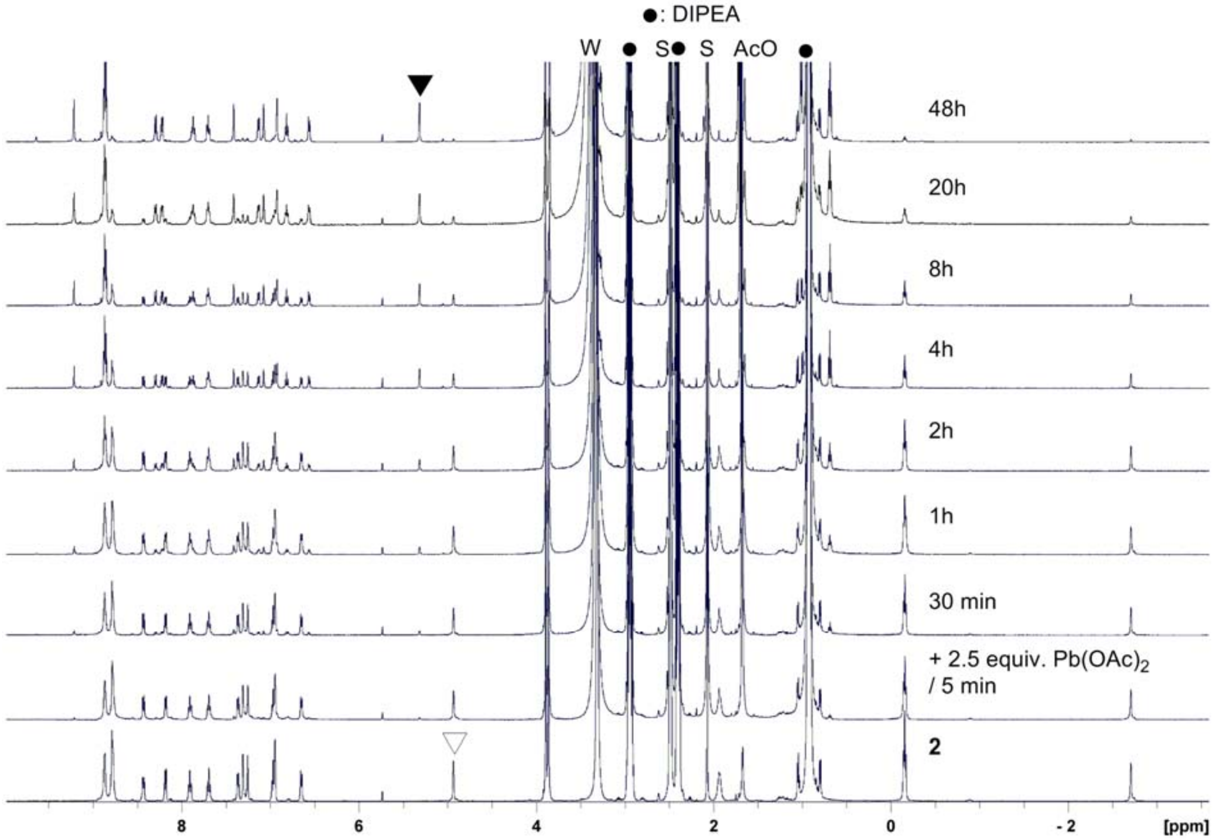
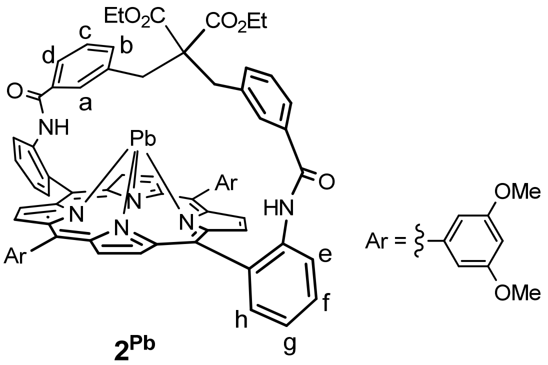


Figure S22. ^{1}H NMR monitoring for the insertion of Pb(II) into **2** (DMSO-d_6, 500 MHz, 15 equiv. DIPEA, 298 K). ▽: **2**; ▼: **2^{Pb}**. S = solvent, W = water.



2^{Pb}

2^{Pb}: ^{1}H NMR (DMSO-d_6, 298 K, 500 MHz, 15 equiv. DIPEA) δ = 9.21 (2H, s, NHCO), 8.86 (8H, m, βpyr), 8.29 (2H, d, J = 7.5 Hz, Hh), 8.22 (2H, d, J = 7.4 Hz, He), 7.86 (2H, t, J = 7.7 Hz, Hg), 7.70 (2H, t, J = 7.6 Hz, Hf), 7.41 (2H, s, HAr), 7.13 (2H, d, J = 7.4 Hz, Hd), 7.07 (2H, s, HAr), 6.92 (2H, s, HAr), 6.81 (2H, t, J = 7.7, Hz Hc), 6.56 (2H, d, J = 7 Hz, Hb), 5.31 (2H, s, Ha), 3.89 (6H, s, OMe), 3.85 (6H, s, OMe), 3.27 (4H, m, CH_2CH_3), 1.65 (s, 4H, CH_2 benz), 0.68 (6H, t, J = 6.6 Hz, CH_2CH_3).

HRMS (ESI-TOF) measurements (positive ion mode), m/z calcd for $C_{71}H_{58}N_6O_{10}NaPb$: 1385.3878 [**2**-2H+Pb+Na]$^+$; found : 1385.3880.

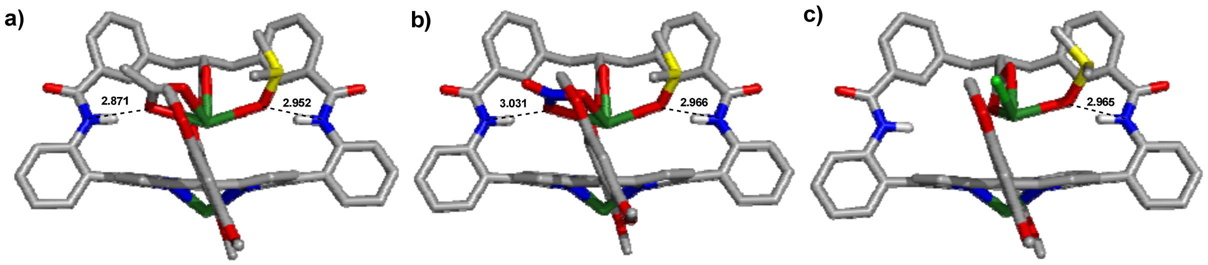


Figure S23. DFT optimized structures (stick views) of (a) **1_{Pb}.PbOAc**, (b) **1_{Pb}.PbNO$_3$** and (c) **1_{Pb}.PbCl**. Non-acidic hydrogen atoms removed for clarity, dashed lines indicate H-bonding interactions (distances in Å). Grey: carbon; blue: nitrogen; red: oxygen; white: hydrogen; yellow: sulfur; deep green: lead; light green: chloride. Total energy and cartesian coordinates of the optimized complexes are given at the end of the Supporting Information.

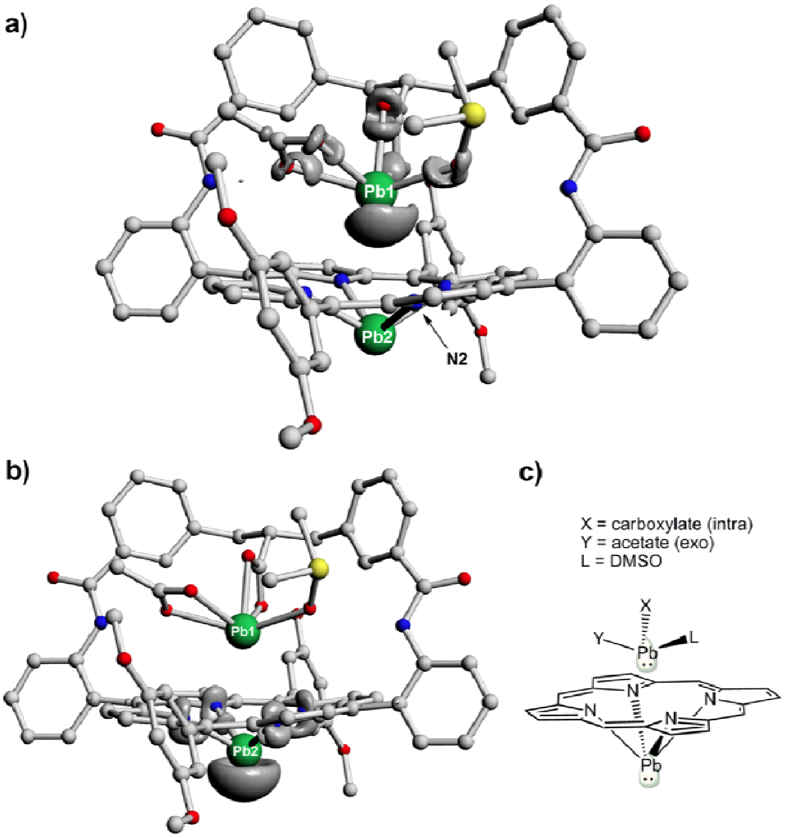


Figure S24. DFT-optimized structure of **1_{Pb}.PbOAc** (hydrogen atoms removed for clarity), represented together with the deformation electron-density isosurface for the coordination sphere of Pb1 (a) and Pb2 (b) (contour value: +0.008 e/bohr^3). (c) Structural type observed for **1_{Pb}.PbOAc** (second coordination sphere omitted).

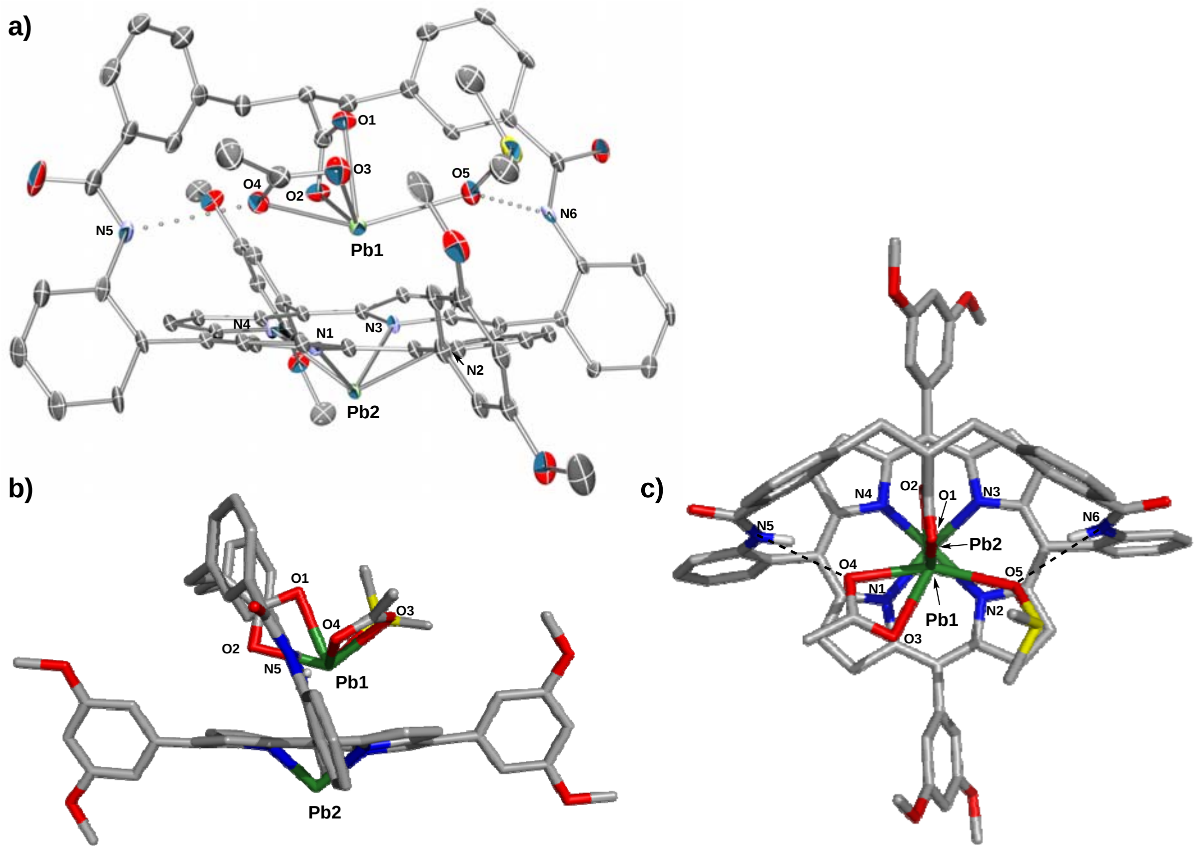


Figure S25. X-ray crystal structure of **1$_{Pb}$.PbOAc**, hydrogen atoms omitted for clarity: (a) ORTEP view drawn with thermal ellipsoids at 30 % probability level; (b) side and (c) apical views, stick representations (NH protons depicted, dashed lines indicate H-bonds).

Crystal data for 1$_{Pb}$.PbOAc: ($C_{70}H_{58}N_6O_{11}Pb_2S$); CCDC 845672; *M* = 1605.66. APEXII, Bruker-AXS diffractometer, Mo$_{K\alpha}$ radiation (λ = 0.71073 Å), *T* = 150(2) K; monoclinic *P*2$_1$/*c*, a = 13.0119(8), b = 12.7579(7), c = 41.322(2) Å, β = 90.465(3) °, *V* = 6859.4(7) Å^3, *Z* = 4, *d* = 1.555 g.cm^{-3}, μ = 4.994 mm^{-1}. The structure was solved by direct methods using the *SIR97* program,[7] and then refined with full-matrix least-square methods based on F^2 (*SHELXL-97*)[8] with the aid of the *WINGX*[9] program. The contribution of the disordered solvents to the calculated structure factors was estimated following the *BYPASS* algorithm,[10] implemented as the *SQUEEZE* option in *PLATON*.[11] A new data set, free of solvent contribution, was then used in the final refinement. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. A final refinement on F^2 with 15654 unique intensities and 691 parameters converged at $\omega R(F^2)$ = 0.1894 ($R(F)$ = 0.0912) for 12855 observed reflections with $I > 2\sigma(I)$.

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[7] A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Crystallogr.,* 1999, **32**, 115.

[8] G. M. Sheldrick, *Acta Crystallogr. Sect. A,* 2008, **A64**, 112.

[9] L. J. Farrugia, *J. Appl. Crystallogr.,* 1999, **32**, 837.

[10] P. Van der Sluis and A. L. Spek, *Acta Crystallogr. Sect. A,* 1990, **46**, 194.

[11] A. L. Spek, *J. Appl. Crystallogr.,* 2003, **36**, 7.

Structural data for 1_{Pb}.PbOAc:

Empirical formula	C_{70} H_{58} N_6 O_{11} Pb_2 S
Formula weight	1605.66
Temperature	150(2) *K*
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, *P* 2_1/*c*
Unit cell dimensions	a = 13.0119(8) Å, alpha = 90 °
	b = 12.7579(7) Å, beta = 90.465(3) °
	c = 41.322(2) Å, gamma = 90 °
Volume	6859.4(7) $Å^3$
Z, Calculated density	4 , 1.555 (g.cm^{-3})
Absorption coefficient	4.994 mm^{-1}
F(000)	3152
Crystal size	0.33 x 0.21 x 0.06 mm
Crystal color	green
Theta range for data collection	2.94 to 27.49 °
h_min, h_max	-16 , 15
k_min, k_max	-16 , 14
l_min, l_max	-53 , 53
Reflections collected / unique	56791 / 15654 [R(int) = 0.0532]
Completeness to theta_max	0.994
Absorption correction type	multi-scan
Max. and min. transmission	0.741 , 0.495
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	15654 / 0 / 691
Goodness-of-fit	1.141
Final *R* indices [I>2σ]	$R1^a$ = 0.0912, $wR2^b$ = 0.1894
R indices (all data)	$R1^a$ = 0.1069, $wR2^b$ = 0.1949
Largest diff. peak and hole	7.299 and -9.697 e.$Å^{-3}$

$^aR1 = \sum | |F_o| - |F_c| | / \sum |F_o|$

$^bwR2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$

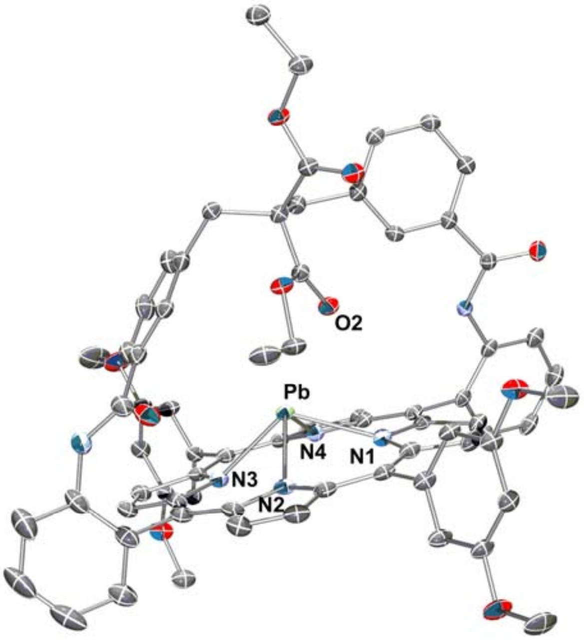

Figure S26. X-ray crystal structure of $\mathbf{2}^{\mathbf{Pb}}$, ORTEP view (30 % probability level, hydrogen atoms omitted). Distances [Å]: Pb to 24-atom mean plane 1.319, Pb-N1 2.369, Pb-N2 2.395, Pb-N3 2.379, Pb-N4 2.399, Pb-O2 3.162.

Crystal data for $\mathbf{2}^{\mathbf{Pb}}$: (C_{71} H_{58} N_6 O_{10} Pb_1); CCDC 855999; *M* = 1362.43. APEXII, Bruker-AXS diffractometer, $Mo_{K\alpha}$ radiation (λ = 0.71073 Å), *T* = 150(2) K; trigonal *R*-3 (I.T.#148), a = 51.1835(13), c = 16.2681(4) Å, *V* = 36908.6(13) $Å^3$, *Z* = 18, *d* = 1.103 $g.cm^{-3}$, μ = 2.107 mm^{-1}. The structure was solved by direct methods using the *SIR97* program,[7] and then refined with full-matrix least-square methods based on F^2 (*SHELXL-97*)[8] with the aid of the *WINGX*[9] program. The contribution of the disordered solvents to the calculated structure factors was estimated following the *BYPASS* algorithm[10], implemented as the *SQUEEZE* option in *PLATON.*[11] A new data set, free of solvent contribution, was then used in the final refinement. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions. A final refinement on F^2 with 18693 unique intensities and 799 parameters converged at $\omega R(F^2)$ = 0.0925 ($R(F)$ = 0.0402) for 12472 observed reflections with $I > 2\sigma(I)$.

Structural data for $\mathbf{2}^{\mathbf{Pb}}$

Empirical formula	C_{71} H_{58} N_6 O_{10} Pb_1
Formula weight	1362.43
Temperature	150(2) *K*
Wavelength	0.71073 Å
Crystal system, space group	trigonal, *R -3*
Unit cell dimensions	a = 51.1835(13) Å, alpha = 90 °
	b = 51.1835 Å, beta = 90 °
	c = 16.2681(4) Å, gamma = 120 °
Volume	36908.6(13) $Å^3$
Z, Calculated density	18 , 1.103 ($g.cm^{-3}$)
Absorption coefficient	2.107 mm^{-1}
F(000)	12384

Crystal size	0.2 x 0.2 x 0.2 mm
Crystal color	green
Theta range for data collection	3 to 27.49 °
h_min, h_max	-66 , 58
k_min, k_max	-66 , 65
l_min, l_max	-18 , 20
Reflections collected / unique	64886 / 18693 [R(int) = 0.0641]
Completeness to theta_max	0.993
Absorption correction type	multi-scan
Max. and min. transmission	0.656 , 0.464
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	18693 / 0 / 799
Goodness-of-fit	0.924
Final R indices [I>2σ]	$R1^a$ = 0.0402, $wR2^b$ = 0.0925
R indices (all data)	$R1^a$ = 0.0688, $wR2^b$ = 0.0998
Largest diff. peak and hole	0.578 and -0.84 e.Å^{-3}

$^aR1 = \sum \left| |F_o| - |F_c| \right| / \sum |F_o|$

$^bwR2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$

Total energy and cartesian coordinates of the complexes optimized using Gaussian09 at the B88P86/LANL2DZ level of theory.

- 1_{Pb}.PbOAc

Energy : -3875.219819 a.u.

Pb	-0.897788	-0.068023	-2.761290
N	0.729565	-1.552973	-1.884792
N	0.809645	1.372440	-1.929529
N	-2.093897	1.472598	-1.404196
N	-2.182843	-1.471219	-1.351529
C	2.105769	-1.388339	-2.126883
C	2.777744	-0.149899	-2.327255
C	2.173565	1.129911	-2.182954
C	2.887706	2.402316	-2.240073
H	3.954876	2.510358	-2.426670
C	1.964873	3.406207	-1.996256
H	2.142719	4.479992	-1.955101
C	0.667321	2.767116	-1.798991
C	-0.543851	3.464673	-1.532642
C	-1.815858	2.851707	-1.343793
C	-3.038802	3.571939	-1.005430
H	-3.109021	4.651699	-0.882674
C	-4.049825	2.633445	-0.866495
H	-5.095028	2.813697	-0.620775
C	-3.457844	1.317126	-1.087999
C	-4.140008	0.074626	-0.934238
C	-3.513838	-1.207021	-0.978934
C	-4.132124	-2.443175	-0.506456
H	-5.157558	-2.527867	-0.148949
C	-3.166973	-3.437473	-0.565253
H	-3.261366	-4.478414	-0.258835
C	-1.946470	-2.832214	-1.089013
C	-0.705536	-3.519104	-1.228902
C	0.528945	-2.915930	-1.602026
C	1.802579	-3.622418	-1.706344
H	1.939870	-4.689453	-1.537081
C	2.770396	-2.684448	-2.029123
H	3.839938	-2.845843	-2.155834
C	4.263115	-0.208889	-2.572684
C	4.762123	-0.684023	-3.818682
H	4.055623	-0.982449	-4.598305
C	6.161268	-0.742237	-4.022233
C	7.070392	-0.346560	-3.005710
H	8.141295	-0.415074	-3.214779
C	6.554775	0.112675	-1.773955
C	5.153120	0.185782	-1.551841
H	4.771957	0.526157	-0.584775
O	6.773943	-1.185218	-5.209028
C	5.896949	-1.609956	-6.308681
H	6.579133	-1.914400	-7.116304
H	5.254983	-0.775808	-6.653335
H	5.264337	-2.467914	-6.007903
O	7.350893	0.520554	-0.689316
C	8.809694	0.470875	-0.858912
H	9.220170	0.831700	0.095866
H	9.139578	1.132998	-1.683242
H	9.155914	-0.563823	-1.050208
C	-5.601655	0.107461	-0.569106
C	-6.561685	-0.430961	-1.452067
H	-6.269203	-0.854523	-2.417301
C	-7.938834	-0.407411	-1.098763
C	-8.361999	0.137604	0.132994
H	-9.410752	0.172564	0.439790
C	-7.384039	0.666780	1.016463
C	-6.010283	0.660228	0.680727
H	-5.249714	1.051455	1.362592

O	-8.806298	-0.957712	-2.057200
C	-10.244176	-0.959106	-1.754238
H	-10.719177	-1.423626	-2.631000
H	-10.626539	0.071925	-1.621449
H	-10.461850	-1.557254	-0.847651
O	-7.905158	1.177788	2.219876
C	-6.957306	1.767363	3.175405
H	-7.577314	2.109592	4.017343
H	-6.420532	2.627107	2.729532
H	-6.224054	1.016275	3.528899
C	-0.496344	4.971193	-1.497958
C	-1.090244	5.660339	-2.589027
H	-1.549913	5.063752	-3.386015
C	-1.080657	7.068769	-2.679064
H	-1.538043	7.570954	-3.538833
C	-0.466832	7.810368	-1.643816
H	-0.444526	8.905888	-1.686479
C	0.118246	7.157809	-0.538747
H	0.581495	7.728196	0.267688
C	0.118723	5.731580	-0.443280
N	0.714589	5.053544	0.666643
H	0.468294	4.047229	0.812017
C	1.471011	5.650466	1.684297
O	1.578317	6.913048	1.847127
C	2.211819	4.731442	2.631028
C	2.844936	3.525637	2.227220
H	2.728195	3.161422	1.199028
C	3.665783	2.798598	3.131983
C	3.816266	3.283623	4.458165
H	4.453187	2.732319	5.163138
C	3.178247	4.476149	4.872474
H	3.312772	4.844339	5.896363
C	2.392469	5.207381	3.958069
H	1.938352	6.164228	4.237117
C	4.371750	1.509776	2.715895
H	5.361966	1.445868	3.209465
H	4.543000	1.492380	1.624079
C	-0.715758	-5.006488	-0.990278
C	-1.398226	-5.812272	-1.940251
H	-1.883560	-5.310785	-2.785796
C	-1.441519	-7.218982	-1.834049
H	-1.967242	-7.814129	-2.589003
C	-0.789073	-7.838606	-0.743858
H	-0.803646	-8.929827	-0.637600
C	-0.116900	-7.066430	0.226729
H	0.381897	-7.541562	1.072324
C	-0.068465	-5.642611	0.124780
N	0.598152	-4.839900	1.108042
H	0.352604	-3.825475	1.137622
C	1.418960	-5.318254	2.136073
O	1.573791	-6.557570	2.403497
C	2.166766	-4.305254	2.980525
C	2.373223	-4.669368	4.339988
H	1.936064	-5.606190	4.701533
C	3.168789	-3.861354	5.179092
H	3.326157	-4.146513	6.225908
C	3.794523	-2.705130	4.656757
H	4.442262	-2.097196	5.302405
C	3.624261	-2.332528	3.296509
C	2.788761	-3.133891	2.468253
H	2.661962	-2.860691	1.413053
C	4.333923	-1.086272	2.770532
H	4.466120	-1.139790	1.674377
H	5.341260	-1.011062	3.226627
Pb	-0.203612	0.055550	0.906945
C	2.242761	0.221308	2.330437
O	2.276502	0.207807	1.017689
O	1.089254	0.199555	2.959964
C	3.556061	0.232746	3.102398
H	3.316469	0.261237	4.181854

O	-0.530668	-2.208583	1.826424
S	-1.291569	-2.734234	3.300175
C	-2.875978	-1.671835	3.327552
H	-3.438814	-1.968566	2.429556
H	-2.586680	-0.607674	3.286195
H	-3.430894	-1.925693	4.245885
C	-0.318761	-1.878918	4.709275
H	0.499749	-2.565961	4.969979
H	-1.015036	-1.741357	5.552881
H	0.075527	-0.928274	4.310409
O	-0.278823	2.484550	1.476268
O	-1.776886	1.162310	2.568788
C	-1.231263	2.339459	2.377202
C	-1.668454	3.540266	3.197547
H	-2.527620	3.284819	3.836435
H	-1.928757	4.381126	2.530943
H	-0.824593	3.870463	3.830615

- 1$_{Pb}$.PbNO$_3$

Energy : -3927.052717 a.u.

C	2.620837	-3.091053	2.600063
C	2.040569	-4.331080	2.984513
C	2.129156	-4.753996	4.339785
C	2.763475	-3.936921	5.299063
C	3.347191	-2.710076	4.904986
C	3.296533	-2.276791	3.552859
C	1.457729	-5.345233	2.018994
O	1.668717	-6.584427	2.242043
C	3.972082	-0.962350	3.164982
C	3.082708	0.296487	3.454680
C	1.858990	0.233769	2.552332
O	0.646822	0.118886	3.042409
Pb	-0.325319	-0.071578	0.790466
O	-2.309181	0.929555	2.128753
N	-1.862944	2.206730	2.072863
O	-2.522377	3.181019	2.568448
N	0.709475	-4.865968	0.937479
C	0.174048	-5.656208	-0.132547
C	-0.402479	-5.000952	-1.275149
C	-0.968466	-5.792838	-2.309135
C	-0.958424	-7.203433	-2.259197
C	-0.371417	-7.840831	-1.142310
C	0.182658	-7.083252	-0.088798
C	-0.429867	-3.505732	-1.452061
C	0.809992	-2.842155	-1.672585
N	0.984983	-1.457302	-1.862148
C	2.372931	-1.240539	-1.977482
C	3.070353	-2.518158	-1.882800
C	2.111464	-3.501406	-1.696388
Pb	-0.610207	-0.013275	-2.882226
N	-1.961095	-1.499936	-1.602999
C	-3.316940	-1.286904	-1.280901
C	-3.923499	-2.560146	-0.903680
C	-2.932988	-3.528616	-0.972032
C	-1.702427	-2.866707	-1.390280
C	3.018057	0.022980	-2.079473
C	4.520836	0.021624	-2.194443
C	5.138818	-0.364636	-3.417535
C	6.551232	-0.360938	-3.505864
C	7.356863	0.007653	-2.396155
C	6.724245	0.378231	-1.189338
C	5.306829	0.390283	-1.082867
C	-3.974492	-0.024175	-1.199732
C	-5.411176	-0.021755	-0.744942
C	-6.440118	-0.548497	-1.552696
C	-7.780569	-0.539324	-1.075846

C	-8.096271	-0.015376	0.196931
C	-7.046965	0.506838	1.000615
C	-5.707750	0.504559	0.547399
O	7.276924	-0.710057	-4.658894
C	6.513689	-1.092562	-5.854862
O	7.411747	0.752669	-0.022205
C	8.880561	0.767797	-0.073281
O	-8.728051	-1.079989	-1.962463
C	-10.133812	-1.087681	-1.535037
O	-7.455535	1.006936	2.248071
C	-6.425525	1.625604	3.102411
N	0.966951	1.468267	-1.866512
C	2.358293	1.277716	-1.973673
C	3.029578	2.573702	-1.936141
C	2.050744	3.542540	-1.787911
C	0.763296	2.856596	-1.742152
C	-0.493269	3.507931	-1.599039
C	-0.509492	5.015475	-1.558214
C	-0.990858	5.691367	-2.710169
C	-1.020646	7.100541	-2.789061
C	-0.565455	7.853478	-1.682194
C	-0.099125	7.212229	-0.515493
C	-0.061978	5.787186	-0.431526
N	0.406113	5.115392	0.739638
C	1.011008	5.710115	1.856076
C	1.624996	4.782779	2.880016
C	2.350654	3.610225	2.538771
C	3.047561	2.871836	3.533111
C	2.979871	3.311265	4.881574
C	2.247839	4.469961	5.231348
C	1.586363	5.213870	4.232573
C	3.859857	1.626772	3.182238
N	-1.964956	1.451942	-1.603391
C	-1.749300	2.842501	-1.518216
C	-3.015229	3.510744	-1.241150
C	-3.988458	2.530008	-1.141565
C	-3.333272	1.240531	-1.339189
O	1.084328	6.970669	2.035726
O	2.038300	0.265245	1.247334
O	-0.655340	-2.326577	1.634699
S	-1.517564	-2.970408	2.999428
C	-0.718970	-2.164547	4.541334
O	-0.680445	2.373551	1.444251
C	-3.147656	-1.982940	2.953256
H	4.106656	2.719240	-2.000256
H	2.183751	4.621223	-1.715443
H	-3.134891	4.584927	-1.110714
H	-5.047024	2.663902	-0.927439
H	-4.963389	-2.687169	-0.605271
H	-3.016424	-4.587304	-0.730053
H	2.270628	-4.571634	-1.572363
H	4.151830	-2.640212	-1.923511
H	4.511136	-0.642701	-4.268812
H	8.443158	-0.010080	-2.517909
H	4.836623	0.669899	-0.135612
H	7.273610	-1.312996	-6.619196
H	5.865516	-0.262677	-6.198101
H	5.898493	-1.994246	-5.667130
H	9.197465	1.087858	0.930318
H	9.246476	1.488427	-0.830510
H	9.283631	-0.240450	-0.291953
H	-6.234512	-0.946788	-2.550672
H	-9.115344	0.013946	0.591945
H	-4.889967	0.887385	1.166172
H	-10.682594	-1.548062	-2.369965
H	-10.505852	-0.058824	-1.362426
H	-10.270138	-1.691951	-0.616654
H	-6.969202	1.971571	3.993828
H	-5.942905	2.482050	2.595954
H	-5.650481	0.890842	3.392601

H	-1.329293	5.086655	-3.560059
H	-1.388818	7.595592	-3.694519
H	-0.579385	8.949343	-1.716224
H	0.237159	7.789733	0.347051
H	0.165142	4.113649	0.836619
H	2.410649	3.285389	1.491951
H	3.520910	2.753249	5.657848
H	2.209925	4.801370	6.275593
H	1.055260	6.140731	4.473300
H	4.791980	1.603507	3.781403
H	4.149838	1.640809	2.115545
H	-1.402995	-5.277191	-3.173559
H	-1.393128	-7.788122	-3.077481
H	-0.346092	-8.935180	-1.080087
H	0.630653	-7.572735	0.776874
H	0.411859	-3.867912	0.977232
H	1.731395	-5.738967	4.606249
H	2.830310	-4.267533	6.342117
H	3.871959	-2.093323	5.646530
H	2.591859	-2.773560	1.550170
H	4.230431	-0.956453	2.090157
H	4.914639	-0.847750	3.736290
H	2.735889	0.276477	4.504683
H	-3.596725	-2.198544	1.972361
H	-2.918098	-0.910577	3.054598
H	-3.783588	-2.354766	3.773143
H	0.109901	-2.825162	4.834674
H	-1.494153	-2.118721	5.324052
H	-0.346596	-1.169787	4.239435

- **1$_{Pb}$.PbCl**

Energy : -3661.740665 a.u.

C	2.318782	-3.373396	2.308741
C	1.676282	-4.585659	2.681494
C	1.780448	-5.049968	4.020479
C	2.495121	-4.297174	4.976163
C	3.135989	-3.095594	4.594133
C	3.066012	-2.623198	3.255855
C	0.986390	-5.505814	1.698296
O	1.057454	-6.768786	1.864662
C	3.805163	-1.345830	2.868617
C	3.084913	-0.028591	3.334993
C	1.789781	0.117973	2.536458
O	0.646412	-0.260220	3.101821
Pb	-0.770336	-0.173848	1.214771
Cl	-2.834427	0.554120	2.813866
N	0.302206	-4.895605	0.640254
C	-0.264642	-5.546266	-0.500242
C	-0.735186	-4.744306	-1.595740
C	-1.319279	-5.391406	-2.716047
C	-1.430210	-6.797439	-2.789562
C	-0.949170	-7.578747	-1.713673
C	-0.378065	-6.966348	-0.577734
C	-0.630634	-3.240114	-1.626461
C	0.666166	-2.666247	-1.777607
N	0.959492	-1.296168	-1.902172
C	2.358411	-1.183789	-1.986430
C	2.950805	-2.519063	-1.927574
C	1.912905	-3.428532	-1.804443
Pb	-0.509295	0.346037	-2.755876
N	-1.970746	-1.102992	-1.570651
C	-3.323271	-0.800794	-1.309468
C	-4.060800	-2.045438	-1.117163
C	-3.154821	-3.088781	-1.241783
C	-1.846499	-2.503629	-1.518111
C	3.108613	0.026955	-2.048884

C	4.602414	-0.100662	-2.202710
C	5.143029	-0.580525	-3.430416
C	6.546192	-0.697109	-3.569151
C	7.421942	-0.356209	-2.504599
C	6.867666	0.109134	-1.292434
C	5.461024	0.241353	-1.136453
C	-3.870785	0.505569	-1.142156
C	-5.346084	0.600051	-0.846481
C	-6.297684	0.305670	-1.846102
C	-7.683904	0.393096	-1.540675
C	-8.121186	0.759760	-0.249151
C	-7.148074	1.042430	0.747351
C	-5.764374	0.968326	0.464354
O	7.194671	-1.147992	-4.732829
C	6.354449	-1.512513	-5.882214
O	7.626427	0.470347	-0.166034
C	9.088796	0.364918	-0.267835
O	-8.547621	0.090543	-2.609408
C	-9.992439	0.177255	-2.359756
O	-7.676780	1.384739	2.002849
C	-6.717789	1.741923	3.064885
N	1.199255	1.639101	-1.767927
C	2.561979	1.332646	-1.893349
C	3.343042	2.567429	-1.805085
C	2.450971	3.605275	-1.592875
C	1.108990	3.021922	-1.553353
C	-0.089684	3.754930	-1.312249
C	0.002989	5.260227	-1.220629
C	-0.491781	6.023035	-2.309746
C	-0.458621	7.435090	-2.303560
C	0.072346	8.103070	-1.175617
C	0.566020	7.375118	-0.072457
C	0.546293	5.949678	-0.084837
N	1.054762	5.181482	1.004927
C	1.553100	5.651565	2.228665
C	2.168373	4.618124	3.142404
C	2.752701	3.404712	2.689026
C	3.380471	2.513846	3.599165
C	3.406141	2.853666	4.977797
C	2.827627	4.059917	5.437562
C	2.217931	4.944166	4.524129
C	4.007627	1.210166	3.116509
N	-1.723876	1.822851	-1.358137
C	-1.390327	3.180783	-1.187050
C	-2.593571	3.929607	-0.833561
C	-3.647849	3.031609	-0.801671
C	-3.109757	1.711521	-1.117584
O	1.501654	6.875372	2.577382
O	1.819553	0.541101	1.308346
O	-0.978144	-2.426008	1.664999
S	-1.594323	-3.264441	3.067079
C	-1.248413	-2.114948	4.552181
C	-3.472450	-2.998052	2.869586
H	4.426990	2.628641	-1.884685
H	2.676673	4.664937	-1.477132
H	-2.621308	4.997550	-0.622156
H	-4.689839	3.235901	-0.562382
H	-5.123628	-2.104674	-0.886826
H	-3.347315	-4.156034	-1.138106
H	1.984452	-4.512227	-1.723745
H	4.019482	-2.727451	-1.951441
H	4.463219	-0.834833	-4.248425
H	8.497779	-0.467771	-2.663554
H	5.059938	0.594453	-0.182106
H	7.061406	-1.833794	-6.661419
H	5.769084	-0.643493	-6.240956
H	5.669781	-2.345452	-5.629394
H	9.467263	0.699992	0.709221
H	9.482134	1.021517	-1.068360
H	9.402810	-0.680723	-0.454680

H	-5.993133	0.027269	-2.859401
H	-9.177771	0.837074	0.021290
H	-5.004280	1.150278	1.231483
H	-10.463807	-0.088060	-3.317841
H	-10.287606	1.203971	-2.066876
H	-10.307859	-0.538222	-1.574897
H	-7.340852	1.968650	3.942878
H	-6.123459	2.630643	2.780027
H	-6.030023	0.905031	3.287635
H	-0.903435	5.486408	-3.172534
H	-0.843381	7.999065	-3.160416
H	0.100615	9.198641	-1.145583
H	0.955530	7.883866	0.810829
H	1.040758	4.164871	0.872555
H	2.761111	3.140870	1.623189
H	3.895971	2.177058	5.690818
H	2.860756	4.312918	6.503572
H	1.789330	5.897794	4.849571
H	4.959950	1.026011	3.652897
H	4.238288	1.276292	2.037432
H	-1.671344	-4.768848	-3.547020
H	-1.876856	-7.269722	-3.671567
H	-1.020345	-8.672257	-1.749616
H	-0.010543	-7.563199	0.258686
H	0.093136	-3.884146	0.748909
H	1.326159	-6.012948	4.277321
H	2.574475	-4.656852	6.008740
H	3.717201	-2.529521	5.334233
H	2.280221	-3.031116	1.266506
H	3.947120	-1.290475	1.772796
H	4.812880	-1.348787	3.330810
H	2.819045	-0.118994	4.404778
H	-3.752078	-3.526014	1.946901
H	-3.644501	-1.911556	2.788859
H	-3.966622	-3.438351	3.751444
H	-0.199213	-1.798030	4.445716
H	-1.421208	-2.719812	5.456995
H	-1.908877	-1.236565	4.473240