Metalloporphyrins

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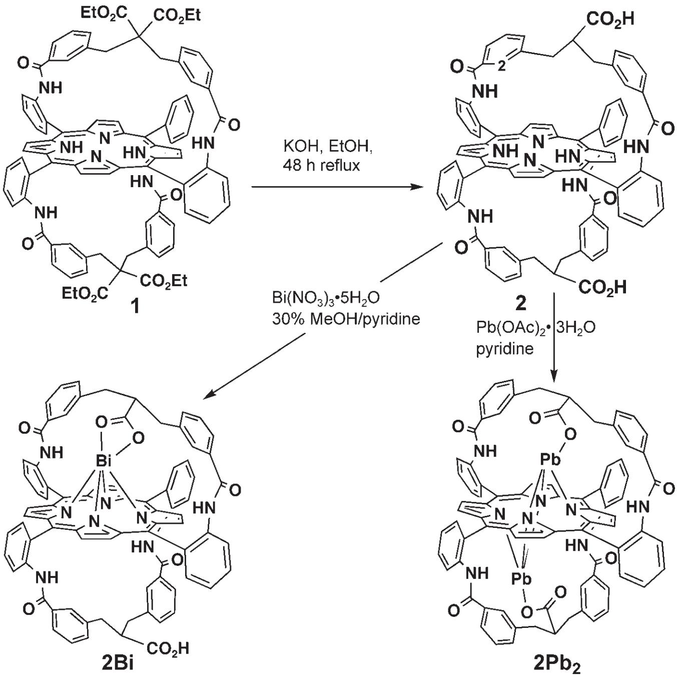
Bismuth and Lead Hanging-Carboxylate Porphyrins: An Unexpected Homobimetallic Lead(II) Complex**

*Zakaria Halime, Mohammed Lachkar, Thierry Roisnel, Eric Furet, Jean-François Halet, and Bernard Boitrel**

The chemistry of post-transition elements such as Ga, In, Tl, Pb, and Bi has been somewhat neglected as compared to that of the transition elements.[1] The chemistry of bismuth has become of increasing interest as its ^{212}Bi and ^{213}Bi isotopes have some potential in cancer therapy.[2] However, the short half-life of the former (1 h) gave birth to the concept of an in situ generator based on the initial complexation of lead.[3] In this Pb/Bi generator, the ^{212}Pb (half-life 10.6 h) in a chelate complex undergoes β emission to give the ^{212}Bi (the direct radioactive daughter) complex of the same chelator.[4] Such a generator requires a chelator that can rapidly coordinate both Pb^{II} and its isoelectronic neighbor Bi^{III}. As it was shown that a porphyrin bearing a pendant carboxylate group can complex bismuth almost instantaneously under very mild conditions,[5] we turned our attention to this type of ligand.[6] However, X-ray structure analyses of Bi^{III} porphyrins are rather scarce,[7] and those of Pb^{II} porphyrins are even more uncommon.[8] This prompted us to design a porphyrin that could coordinate both elements, and which presumably exhibits a chelate effect,[9] owing to the addition of a strap bearing a carboxylate group.[10] Herein we report the crystal structures of both bismuth and lead complexes of such a ligand, the latter of which exhibits an unexpected mononuclear homobimetallic structure.

Earlier, we reported the synthesis and crystal structure of porphyrin **1**, bearing an ethyl malonyl residue in both apical positions owing to 5,15 straps.[10] The two sides of the porphyrin were identically functionalized to avoid any selectivity in coordination chemistry and for synthetic convenience. Porphyrin **1** was quantitatively transformed into **2**, in which a carboxylate group hangs over each side of the macrocycle (Scheme 1).



Scheme 1. Synthesis of hanging-carboxylate porphyrins.

In **1**, the distance between the centroid of the four nitrogen atoms of the porphyrin and the carbonyl oxygen atom of the closest ester group is 3.111 Å. In the only crystal structure of a mononuclear bismuth porphyrin reported so far, in which the carboxylate group is bound to bismuth in an η^2 mode, the distances between the centroid of the four nitrogen atoms and the two carboxylate oxygen atoms are 3.591 and 3.658 Å. Thus, without any coordinative driving force, at least one of the two oxygen atoms of a carboxy group in **2** is close enough to establish a bond with a metal such as bismuth known to coordinate approximately 1.2 Å out of the plane of the porphyrin.

Bismuth insertion was achieved at room temperature by stirring 1 equiv of $Bi(NO_3)_3 \cdot 5H_2O$ with a solution of **2** in MeOH and pyridine for 5 min. The fact that in contrast to this, even in refluxing pyridine, bismuth insertion was not observed in precursor porphyrin **1** is consistent with internal coordination of the hanging carboxylate group. This argument is reinforced by comparison of the ^{1}H NMR spectra of **2** and **2Bi**, particularly for protons H2 (for atom labeling, see upper

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[*] Dr. Z. Halime, Dr. T. Roisnel, Dr. E. Furet, Dr. J.-F. Halet, Dr. B. Boitrel
Université de Rennes1—Ecole Nationale Supérieure de Chimie de Rennes
Sciences Chimiques de Rennes, UMR CNRS 6226
35042 Rennes Cedex (France)
Fax: (+33) 2-2323-5637
E-mail: bernard.boitrel@univ-rennes1.fr

Prof. Dr. M. Lachkar
Laboratoire d'Ingénierie des Matériaux
Organométalliques et Moléculaires (LIMOM)
Faculté des Sciences Dhar El Mehraz
Université Sidi Mohammed Ben Abdellah
B.P. 1796 (Atlas), 30000 Fès (Morocco)

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strap of porphyrin **2** in Scheme 1). In free-base porphyrin **2**, these four protons appear as two singlets ($\delta = 5.05$ and 5.01 ppm) since the two protons of each strap are not magnetically equivalent, whereas in **2Bi**, these four protons give rise to four singlets ($\delta = 5.59$, 5.41, 4.96, and 4.87 ppm). This indicates that the two straps are no longer equivalent in **2Bi** and is consistent with coordination of one strap through its carboxylate group. This potential coordination was also investigated by IR spectroscopy, but no conclusion could be drawn due to other CO bands from the amide groups of the compound. This intramolecular coordination was confirmed by the crystal structure analysis of **2Bi** (Figure 1 a), which crystallizes from acetone/water/DMSO as green cubic crystals in the triclinic space group $P\bar{1}$.[11]

This complex is the second example of a mononuclear bismuth porphyrin with an intramolecular counteranion.[5] The main structural feature of all known bismuth porphyrins is the large displacement of the metal from the 24-atom mean porphyrin plane (av 1.255 Å based on known structures). In **2Bi**, the metal atom lies 1.309 Å above the mean plane, the largest such displacement reported so far.

This larger displacement is presumably due to linkage of the carboxylate group to the strap. However, this strap exhibits some flexibility, as shown by the two different conformations found in **2Bi**: the carboxy group of the noncoordinating strap (depicted in black in Figure 2, left) is oriented outside the cavity of the porphyrin, while the coordinating carboxylate group of the other strap is locked inside the cavity by the "W shape" of the strap. The bismuth atom is seven-coordinate with four Bi–N bonds to the macrocycle, two bonds with the oxygen atoms of the carboxylate group (2.925 and 2.367 Å), and a bond to a DMSO molecule (2.587 Å) of crystallization. As a result of the coordination of the carboxylate group, the bismuth atom is slightly displaced from its apical position towards the carboxylate group, as indicated by the Bi–N1 (2.279 Å) and Bi–N2 (2.323 Å) bonds being shorter than Bi–N3 (2.490 Å) and Bi–N4 (2.460 Å). Delocalization over the carboxylate group is not symmetrical (C–O 1.206 and 1.295 Å). The Bi–O3 bond is located close to the apical position of the bismuth atom, and therefore the lone pair of bismuth ($6s^2$) is expected to occupy the vacant coordination site of the polyhedron, as it cannot be in the apical position due to electronic repulsion. In summary, the crystal structure of **2Bi** clearly indicates that the type of strap in **2** is adequate for the coordination of bismuth owing to the ability of the carboxylate group to switch from the "out" (uncoordinated) to the "in" (coordinated) position.

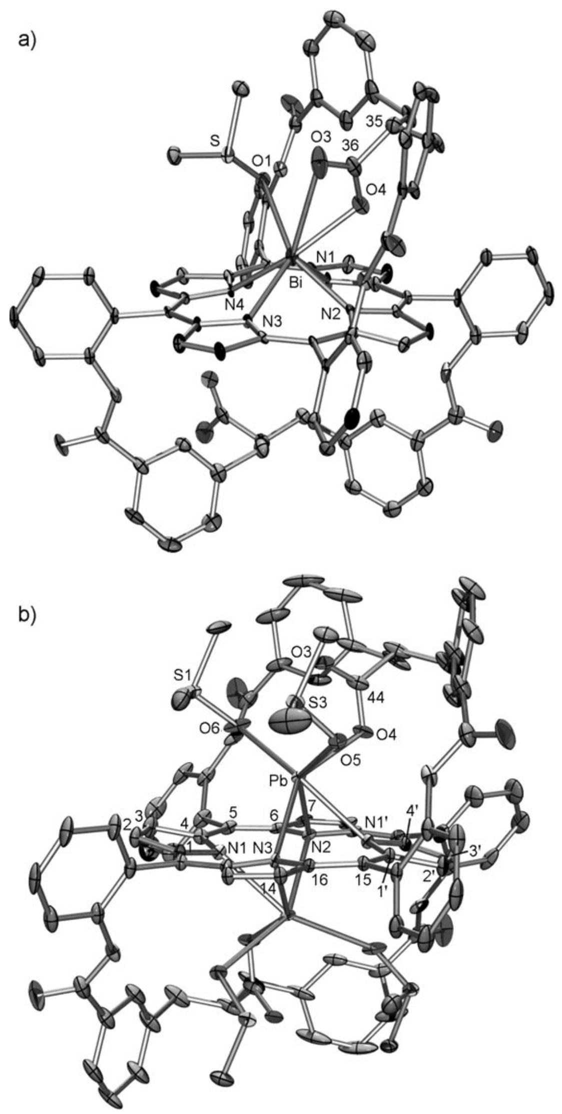

Figure 1. ORTEP views of **2Bi**·DMSO (a) and **2Pb$_2$**·4 DMSO (b) drawn with thermal ellipsoids at the 30% probability level; hydrogen atoms omitted for clarity. Selected distances [Å] and angles [°]: **2Bi**·DMSO: N1-Bi 2.279(4), N2-Bi 2.323(4), N3-Bi 2.490(4), N4-Bi 2.460(4), O1-Bi 2.587(4), O3-Bi 2.925(4), O4-Bi 2.367(4), Bi to 24-atom mean plane 1.309; O3-O4-C36-C35 plane to 24-atom mean plane 73.24; **2Pb$_2$**·4 DMSO: Pb-Pb′ 3.598(3), N1-Pb 2.480(3), N2-Pb 2.787(3), N3-Pb 2.648(3), O4-Pb 2.320(3), O5-Pb 2.651(3), O6-Pb 2.832(3), Pb to 24-atom mean plane 1.795; O3-O4-C36-C34 plane to 24-atom mean plane 88.55, N1-C1-C2-C3-C4 plane to 24-atom mean plane 11.03, N2-Pb-N3-Pb′ plane to 24-atom mean plane 86.04.

Consequently, it was logical to insert lead into **2**. It could be anticipated that in the resulting complex, the bivalent metal would be out-of-plane four-coordinate, as in all reported crystal structures of lead(II) porphyrins,[8] with an average distance between metal atom and mean porphyrin plane of 1.272 Å and the intramolecular carboxy group left in the "out" position. In contrast to the metalation conditions reported in the literature (refluxing DMF, 2 h), **2** was metalated by lead acetate in pyridine after 10 min at room temperature. Surprisingly, the ^{1}H NMR spectrum of the lead porphyrin indicated that the two sides of the macrocycle are identical, as in the free-base porphyrin **2**. Indeed, the H2 protons appear as two singlets at $\delta = 5.90$ and 5.48 ppm as opposed to four singlets in **2Bi**. This could indicate a metal atom disordered over two positions on each side of the porphyrin, as described by Plater et al.[8] However, the high-resolution MS spectrum of the metalloporphyrin revealed a 2:1 ratio of lead to porphyrin. The complex crystallizes in the monoclinic space group $C2/c$ from acetone/water/DMSO.[12] Its bimetallic structure (Figure 1 b) belongs to class III/type M in Buchler's classification of metalloporphyrins.[13] In this class, the complex is mononuclear with regard to the porphyrin, which acts as a bridging ligand between the two

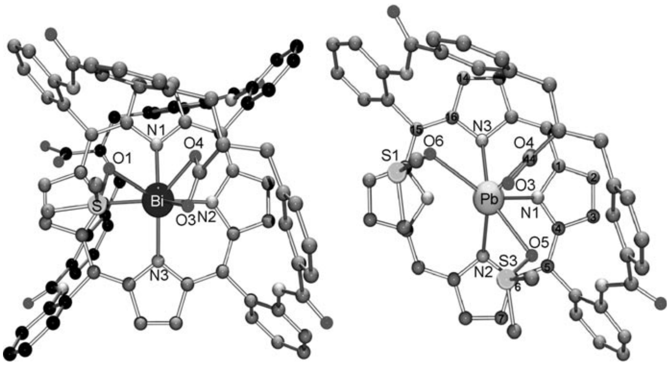

Figure 2. Apical ball-and-stick views of **2 Bi**·DMSO (left, noncoordinating strap in black) and **2 Pb**$_2$·4 DMSO (right, owing to the axial symmetry, one strap is not shown).

metal atoms. Type M, also named *trans*-$(MZ_3)_2(P)$, implies two metal atoms (one above and one below the plane of the porphyrin) bonded to three adjacent nitrogen atoms of the porphyrin and three other bonds with three neutral or negatively charged axial ligands. So far, this specific configuration has only been reported for monovalent metals such as Re, Tc,[14] and Tl.[15] A tridentate porphyrin bonding mode was also reported for tellurium in the mononuclear monometallic Te^{IV} bis-chloro complex of *meso*-tetra-*p*-tolylporphyrin.[16] The crystal structure of **2 Pb**$_2$ is the first example of such an arrangement for a bivalent metal.

Obviously, the porphyrin macrocycle in **2 Pb**$_2$ is significantly distorted according to a pure wave type (Figure S1). This distortion is a direct consequence of the tilting of two opposite pyrrole rings (N1-C1-C2-C3-C4 and N1′-C1′-C2′-C3′-C4′) towards the metal atom to which they are coordinated, with an angle to the mean porphyrin plane of 11.03° (Figure S2). The coordination sphere of each six-coordinate lead atom is an unsymmetrical trigonal antiprism, as shown in Figure 2 (right). It is composed of three nitrogen atoms from the porphyrin (N1, N2, N3), one monohapto carboxylate group (O4), and two DMSO molecules of crystallization (O5 and O6). The plane of the carboxylate group is almost perpendicular (88.55°) to the mean plane of the porphyrin. The N2 and N3 atoms are bonded to both lead ions at distances of 2.787(3) and 2.648(3) Å, respectively, while the N1−Pb bond, as expected, is shorter (2.480 Å). The distance from the metal ion to the uncoordinated fourth nitrogen atom is rather long (2.995(3) Å). On each side, the metal lies 1.795 Å from the mean porphyrin plane. The two metal ions, 3.598(3) Å from each other, are positioned almost over the center of the porphyrin, as opposed to what was reported for $[(tpp)\{Re(CO)_3\}_2]$ (tpp = tetraphenylporphyrin) and $[(oep)\{Tl(thf)\}_2]$ (oep = octaethylporphyrin), in which the metal atoms are more centered above the three adjacent nitrogen atoms. This almost apical position of the two lead atoms is illustrated by the angle of 86.04° between the Pb-N2-N3-Pb′ plane and the mean porphyrin plane, where the C_2 axis is located along the N2−N3 axis.

Interestingly, the trigonal-antiprismatic environment around the Pb atoms in **2 Pb**$_2$ is rather strongly distorted, and some void can be identified in the distribution of bonds. In other words, the coordination geometry of lead is somewhat hemidirected according to the terminology of Glusker et al., with lead-to-ligand bonds directed through only part of the encompassing space.[21] Such a distortion is not uncommon for six-coordinate Pb^{II} complexes.[21] This might reflect some evidence of a “stereochemically active lone pair of electrons”. This phenomenon is often associated with some ionic bonding character between lead and the surrounding ligands. In agreement with this proposal, two Pb−O and three Pb−N bonds are rather long (see above).

To gain some insight into the validity of a stereochemically active lone pair in **2 Pb**$_2$, density functional calculations were carried out at the B88P86/TZP level of theory incorporating scalar relativistic corrections (ZORA).[22] A full (gas-phase) geometry optimization was first performed on **2 Pb**$_2$ within C_2 symmetry. The computed geometry is in overall good agreement with the X-ray experimental data, despite the possible flexibility of the porphyrin straps. Indeed, the asymmetrical six-coordinate environment of each lead atom is kept during the gas-phase optimization process. In particular, no tilting of the carboxylate group, which would lead to a η^2 bonding mode, was observed.

The computed Pb−O(carboxylate) bond is rather short [2.392 vs 2.321 Å (exp)], whereas the Pb−O(DMSO) bonds are long (2.821 and 2.835 Å vs 2.651 and 2.832 Å (exp)] and reflect some ionic bond character. The ordering of Pb−N distances is also preserved, with values of 2.549 Å (+0.069 vs exp), 2.666 Å (+0.018 vs exp), and 2.839 Å (+0.052 vs exp) for Pb−N1, Pb−N3, and Pb−N2, respectively. The computed Pb−Pb distance of 3.668 Å is 0.070 Å longer than the experimentally measured distance. Computation of the Mulliken Pb−Pb overlap population gives a negative value ($-0.18\,e^-$) which suggests that there is no metal–metal bond in **2 Pb**$_2$. Examination of the electron density supports this conclusion: a density hole is clearly identified between the two Pb atoms. Clearly, they are forced by the metal–nitrogen bonds to be close to each other, and their repulsion may induce the observed porphyrin distortion.

Examination of the deformation electron-density map[27] shows some pockets in the vicinity of the lead atoms pointing away from the O and N ligands (Figure 3). We think that this may be associated with the presence of a lone pair of electrons which might favor a hemidirected geometry in **2 Pb**$_2$.

In summary, we have designed a simple strapped porphyrin that can rapidly coordinate both bismuth and lead owing to an internal hanging carboxylate group. The possibility of switching between two extreme positions of the carboxylate group allows coordination of metal ions inside the porphyrin. The unexpected mononuclear bimetallic structure of the lead complex is under investigation for further applications.

Experimental Section

2 Bi: ^1H NMR ([D$_6$]DMSO, 323 K, 500 MHz): $\delta_H = 9.37–8.85$ (m, 14 H; β-pyr + NHCO + ArH), 8.24 (brs, 2 H; ArH), 7.81 (m, 8 H; ArH), 7.50 (m, 4 H; ArH), 7.24–6.71 (m, 10 H; ArH), 5.59 (s, 1 H; H2), 5.41 (s, 1 H; H2), 4.96 (s, 1 H; H2), 4.87 (s, 1 H; H2), 2.22 (brs, 1 H; CH_2 benz), 2.04 (brs, 2 H; CH_2 benz), 1.76 (brs, 1 H; CH_2 benz), 1.29 (m, 3 H; CH_2 benz), 0.93 (brs, 1 H; CH_2 benz), 0.80 (brs, 2 H; CH),

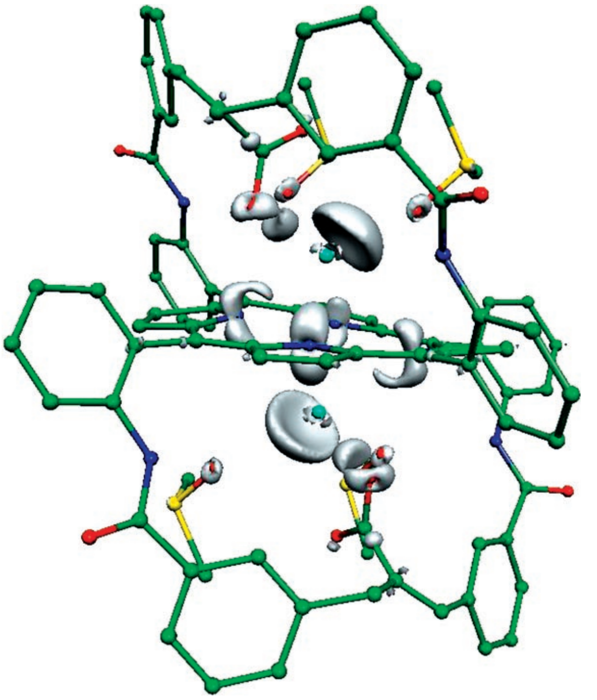

Figure 3. Deformation density isosurface (contour value: +0.01 e bohr^{-3}) of the DFT optimized molecular structure of **2 Pb$_2$**. Pb light blue, S yellow, O red, N dark blue, and C green. Hydrogen atoms are omitted for clarity.

0.48 ppm (brs, 2H; CH); ^{13}C NMR ([D$_6$]DMSO, 323 K, 125 MHz): δ_C = 173.4, 169.1, 136.5, 131.9, 129.5, 127.1, 127.5, 126.1, 125.8, 121.2, 119.9, 42.1, 40.5, 29.5, 28.1 ppm; UV/Vis (DMSO/CHCl$_3$ 10%): λ_{max} [nm] ($10^{-3}\varepsilon$ [dm^{3}mol^{-1}cm^{-1}]): 357 (32.5), 475 (148.8), 605 (8.9), 654 (8.5); ESI-HRMS calcd for $C_{80}H_{56}BiN_8O_8$: *m/z* 1465.4025 [*M*+H]$^+$; found: 1465.4024.

2 Pb$_2$: ^{1}H NMR ([D$_6$]DMSO, 323 K, 500 MHz): δ_H = 9.67 (brs, 4H; NHCO), 9.33 (brs, 2H; β-pyr), 9.24 (brs, 2H; ArH), 9.02 (brs, 2H; ArH), 8.95 (d, *J* = 7.5 Hz, 2H; ArH), 8.86–8.81 (m, 6H; β-pyr), 7.92 (d, *J* = 7.5 Hz, 2H; ArH), 7.88 (t, *J* = 7.5 Hz, 2H; ArH), 7.83 (brs, 2H; ArH), 7.73 (t, *J* = 7.5 Hz, 2H; ArH), 7.54 (brs, 2H; ArH), 7.32 (brs, 2H; ArH), 7.23 (brs, 2H; ArH), 7.04 (brs, 2H; ArH), 6.97 (m, 4H; ArH), 6.88 (brs, 2H; ArH), 5.90 (s, 2H; H2), 5.48 (s, 2H; H2), 2.44 (brs, 2H; CH$_2$ benz), 2.32 (brs, 2H; CH$_2$ benz), 2.21 (brs, 2H; CH$_2$ benz), 1.84 (brs, 2H; CH$_2$ benz), 1.34 ppm (brs, 2H; CH); ^{13}C NMR ([D$_6$]DMSO, 323 K, 125 MHz): δ_C = 172.7, 169.4, 138.4, 136.4, 131.8, 129.0, 127.9, 125.8, 122.8, 120.8, 40.1, 40.5, 29.5 ppm; UV/Vis (DMSO/CHCl$_3$: 10%): λ_{max} [nm] ($10^{-3}\varepsilon$ [dm^{3}mol^{-1}cm^{-1}]): 357 (35.6), 491 (201.6), 647 (9.9), 701 (18.9); ESI-HRMS calcd for $C_{80}H_{54}N_8O_8Pb_2$: *m/z* 1693.3495 [*M*+Na]$^+$; found: 1693.3498.

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[11] Structural data of **2 Bi**: Triclinic $P\bar{1}$, $a = 13.744(3)$, $b = 15.612(4)$, $c = 19.703(5)$ Å, $\alpha = 70.287(13)$, $\beta = 90.043(14)$, $\gamma = 76.838(13)°$, $V = 3861.5(16)$ Å^3, $Z = 2$. Single-crystal X-ray diffraction data were collected at $T = 100$ K on an APEXII Bruker-AXS KappaCCD diffractometer (Mo$_{K\alpha}$ radiation, ω scans). A total of 66618 reflections were integrated to give 17290 independent reflections (13557 observed with $I > 2\sigma(I)$). SADABS[17] semi-empirical absorption corrections based on equivalent reflections ($\mu = 3.418$ mm^{-1}, $T_{min} = 0.471$, $T_{max} = 0.559$) were applied. The structure was solved by direct methods (SIR97)[18] that revealed all non-hydrogen atoms and then refined by a least-squares procedure on F^2 (SHELXL)[19]: $R_1 = 0.0528$, $wR_2 = 0.1426$.[12b]

[12] a) Structural data for **2 Pb$_2$**: Monoclinic $C2/c$, $a = 30.0600(14)$, $b = 15.9477(8)$, $c = 23.5898(10)$ Å, $\beta = 115.047(2)°$, $V = 10245.2(8)$ Å^3, $Z = 4$. Single-crystal X-ray diffraction data were collected at $T = 100$ K on an APEXII Bruker-AXS KappaCCD diffractometer (Mo$_{K\alpha}$ radiation, ω scans). A total of 43993 reflections were integrated to give 11661 independent reflections [9721 observed with $I > 2\sigma(I)$]. SADABS semi-empirical absorption corrections based on equivalent reflections ($\mu = 2.435$ mm^{-1}, $T_{min} = 0.677$, $T_{max} = 0.930$) were applied. The structure was solved by direct methods (SIR97) that revealed all non-hydrogen atoms and then refined by a least-squares procedure on F^2 (SHELXL): $R_1 = 0.0354$, $wR_2 = 0.0957$. The SQUEEZE[20] procedure implemented in PLATON was used to calculate the contribution of the disordered solvent molecules to the observed intensities. The new data set, free of the solvent contribution, was used in the final refinement. b) CCDC-625292 (**2 Bi**) and CCDC-625293 (**2 Pb$_2$**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[22] Density functional calculations were performed with the Amsterdam Density Functional package (ADF2005.1, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com)[23] with Becke's gradient-corrected exchange functional[24] and the gradient-corrected correlation functional of Perdew.[25] Triple-ζ-quality Slater-type orbital basis sets including polarization functions (TZVP) were employed for all atoms to describe valence electrons. Inner shells were kept frozen up to 4d for Pb, 2p for S, and 1s for C, N, and O. Scalar relativistic corrections were taken into account within the zeroth-order regular approximation (ZORA).[26]

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[27] Deformation density isosurfaces were obtained by subtracting from the molecular density of **2Pb$_2$** the self-consistent computed densities of the $[Pb_2]^{4+}$ and $[\text{porphyrin}+4\,\text{DMSO}]^{4-}$ units kept with their respective geometries in the optimized complex. Molecular structures and isosurfaces were drawn with Molekel 4.1 visualization program.[28]

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