Supramolecular Assembly of Diplatinum Species through Weak Pt···Pt Intermolecular Interactions: A Combined Experimental and Computational Study

Line dancing in diplatinum compounds: The effect of temperature, concentration, solvent and the nature of the ligand L in the association of [Pt₂L₄] compounds, which can be followed by UV/Vis spectroscopy (see figure), were studied. Computational simulations show that the broad band at 760 nm appearing at low temperatures and high concentrations is due to the formation of [Pt₂L₄]ₙ supramolecules assembled through weak intermolecular Pt···Pt interactions.
Supramolecular Assembly of Diplatinum Species through Weak Pt$^{II}$···Pt$^{II}$ Intermolecular Interactions: A Combined Experimental and Computational Study

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Abstract: The present study elucidates the factors that govern the spontaneous self-assembly of a family of dimetal [Pt$_2$L$_4$] (L = dithiocarboxylato ligand) complexes. Experimental data show that variables such as temperature, concentration, solvent and the nature of the ligand L have a critical effect on the reversible self-assembly of supramolecular [Pt$_2$L$_4$]$_n$ entities. In solution, new UV/Vis spectroscopic features emerge at low temperatures and/or high concentrations, which are attributed to the formation of oligomeric [Pt$_2$L$_4$]$_n$ species. The description of intermolecular Pt···Pt interactions, the main driving force for the association, was addressed from a computational perspective. The contributions from intermolecular Pt···S and S···S interactions to these supramolecular assemblies were found to be repulsive. Experimental UV/Vis data have been interpreted by means of computational spectroscopy.

Keywords: computational chemistry · density functional calculations · metal–metal interactions · platinum · supramolecular chemistry

Introduction

A main goal in supramolecular chemistry is the understanding of weak intermolecular interactions that can result in self-assembly processes.$^{[1]}$ Although hydrogen bonding has been widely studied, other interactions such as weak metal–metal interactions remain less explored.$^{[2]}$ Among these, the tendency of gold compounds to aggregate through Au–Au bonds is the most familiar phenomenon, known as aurophilicity.$^{[3]}$ However, this is not the only metal–metal supramolecular interaction, and weak d$^{10}$···d$^{10}$ bonding has also been observed for Ag$^{+}$ and Cu$^{2+}$ centres.$^{[4]}$ Similarly, d$^{8}$···d$^{8}$ interactions have been reported for some Pt$^{II}$ compounds. This weak metal–metal interaction can result in columnar stacks formed by one-dimensional chains of aligned coordination complexes (Scheme 1).$^{[5]}$

The linear structures formed by the stacking of square-planar monomer complexes have shown interesting properties. For example, tetracyanoplatinates, K$_2$Pt(CN)$_4$X$_n$·nH$_2$O (X = Cl, Br, n = 3), commonly called KCPs, were one of the first examples showing electrical conductivity.$^{[6]}$ These systems are formed by the stacking of square-planar [Pt(CN)$_4$]$_n$ anion complexes.$^{[7]}$ The structures are formed by

![Scheme 1. Schematic illustration of the columnar structures originating from the stacking of a) square planar mononuclear platinum complexes and b) dinuclear complexes.](image-url)
the overlapping of 5dπ orbitals, which are strongly affected by the Pt–Pt intermolecular distances. The anisotropic conductive properties of the KCPs are connected to their metal–metal distances. The electrical conductivity for the K3[Pt(CN)4] (5 × 10−4 S cm−1) is substantially increased upon partial oxidation of the KCPs. This is related to a shortening of the Pt–Pt distances, which become close to what is found in the platinum metal (2.78 Å). KCP-based materials represent the first inorganic “molecular wires” ever designed.[9] In a similar approach, analogous columnar systems have been formed with dimetallic precursors.[9] These discrete dinuclear complexes with intermolecular metal–metal interactions have fascinating magnetic and electrical properties.[10] Some of them have been shown to be suitable as precursors for weakly bound one-dimensional metal chains.[10] Recently, it has been shown that linear arrangements in crystalline samples of such compounds can result on different conductivity properties, which are highly dependent on the Pt–Pt distances determined by the nature of the dithiocarboxylato ligands. In a previous report, it has been demonstrated that the compound [Pt2(S2C(CH2)5CH3)4] undergoes reversible aggregation processes in solution as observed by a characteristic thermochromic behaviour.[11] More recently, we have reported that such aggregations also occur in compound [Pt2(S2C(CH2)3)4] and that can trigger the formation of nanofibers on surfaces.[10]

A deeper understanding of the chemical principles that direct such assemblies is of great interest due to the potential impact on the bottom-up assembly of conductive 1D nanostructures of these principles. This work aims to provide answers by means of a combination of experimental and theoretical insights to hitherto unexplored points concerning supramolecular assembly. Specifically, the factors (nature of ligands, solvents and other physical parameters) that have an influence on such self-associations are explored. The results observed in solution will be discussed and related with the structures found in the monocrystals. In addition, novel insights on the molecular and electronic structures of supramolecules in solution are presented and related with their spectroscopic features.

**Results and Discussion**

Crystal structure of compounds 1 and 2: All the reported crystal structures of the formula [Pt2L4] show linear arrangements that are directed by intermolecular PtII–PtII interactions.[12] There is only one exception to this tendency for a polymorph reported of [Pt2(S2CCH3)4], which does not show short Pt–Pt distances.[13] In contrast, in this structure Pt–S distances of 3.51 Å can be found. These values were previously interpreted as evidence that Pt–S interactions directed the packing of [Pt2(S2CCH3)4] units. However, such long distance is in the limit of what can be considered as weak interaction and probably is just the result of packing effects in the condensed phase. Below, the possibility of Pt–S interactions are discussed from a theoretical perspective. On the other hand, in the rest of the reported structures, the metal–metal distances fall in the range between 3.08 and 3.39 Å, below the sum of their van der Waals radii (3.5 Å). As shown in Table S2 in the Supporting Information, such distances depend on the nature of the organic fragment attached to the dithiocarboxylate group. Bulkier ligands, such as C6H11−CS2 or (CH3)2CH−CH−CS2−, result in longer intermolecular Pt–Pt distances.

In this work, the crystal structure of two new [Pt2L4] complexes has been determined. In particular two [Pt2L4] (L = C6H5−CS2−) complexes have been studied: one with the linear alkyl chain (CH3(CH2)2−CS2−) and the other with a branched alkyl group ((CH3)2CH−CH−CS2−). The intermolecular Pt–Pt distances observed in these two new structures are very different depending on the steric hindrance imposed by the ligand. Thus, for the complex with the linear alkyl chain a Pt–Pt distance of 3.12 Å is found, whereas for the branched isomer this distance increases up to 3.26 Å. The possible relation of this effect with the behaviour in solution is discussed below.

The crystal structures of compounds 1 and 2 consist of quasi-one-dimensional chains based on collinear alignment of [Pt2(S2CR)4] dinuclear entities with short intra- and interdimeric Pt–Pt distances (Figure 1). The dinuclear entities
show a windmill-shaped arrangement in which four μ-dithiocarboxylato-kS:S' ligands bridge two PtII centres with a metal–metal distance in the range 2.737–2.768 Å. The metal coordination environment consists of four sulphur atoms defining the equatorial plane from which the platinum atoms deviate 0.051–0.064 Å inwards from the dimer. Above and below this plane, there are placed the other platinum atom of the dimer and a platinum atom from the next dinuclear unit. The two PtS4 squares of the dinuclear entity are rotated by 21.72–26.04° from the eclipsed arrangement. The complexes are stacked collinearly along the intradimeric Pt–Pt axis by means of short interdimer Pt–Pt distances: 3.119–3.337 Å. Adjacent PtS4 squares belonging to different dimers are also rotated by 44.08–44.44° for compound 1 and 32.61–38.68° for compound 2. The analysis of the crystal structure of these compounds together with the previously published examples of diplatinum dithiocarboxylate chains suggests that the steric hindrance of the substituents of the dithiocarboxylato ligands influences the interdimeric Pt–Pt distances; the bulkier is the substituent, the longer is the interdimer Pt–Pt distance 3.119 (1) versus 3.268 Å (2).

Supramolecular assembly of compound 3 in CH2Cl2: In addition to the complexes with the novel structures reported herein, we included in this study the complex [Pt2(S2C(CH2)5CH3)4] (3). A crystal structure of this compound has been previously reported in a recent work.[10] In the present study, compound 3 offers the advantage of its high solubility, which allowed the study of self-aggregation in solution in a wide range of concentrations avoiding precipitation processes.

Figure 2 shows the thermochromic behaviour observed in 2-0.2 mM solutions of 3 in CH2Cl2. By decreasing the temperature, a new broad band appears in the red/near-infrared region as observed previously for complexes [Pt2(S2C(CH2)4CH3)4] and [Pt2(S2CCH3)4][11] This is a very wide band that disappears upon heating and re-appears when the solution is cooled down again. The dependence upon the concentration of such absorbance indicates that it is due to reversible aggregation processes in solution. Similar observations for complex [Pt2(S2C(CH2)5CH3)4] were previously proposed as a result of an equilibrium between the species [Pt2L4] and [Pt2L4]−.[11] However, our detailed studies of this phenomenon indicate that a more complex scenario should be considered. In fact, the gradual redshift of the appearing band while decreasing the temperature suggests, according to our theoretical results, that the average size of the supramolecular entities present in solution increases at lower temperatures.

A first attempt to characterise the species [Pt2L4]− (n = 1, 2, ...) present in solution was carried out by means of variable-temperature (VT)1H NMR measurements. Unfortunately, lowering the temperature did not allow us to distinguish signals from different oligomers. The only variation observed in the 1H NMR spectra while decreasing the temperature, is the widening of signals, which is especially dramatic for the signal corresponding to the protons closer to the platinum centres (Figure S1 in the Supporting Information). Such an effect could be explained by the dynamic behaviour of this system that results in fast chemical exchange, together with the expected increase of the viscosity of the solvent at lower temperatures. Accordingly, theoretical calculations performed with the species [Pt2(S2C(CH2)5CH3)4] and [Pt2(S2CCH3)4]2 (see below) suggest that protons remote from the Pt centres by four bonds are insensitive to association processes.

A detailed comparison of UV/Vis features observed in 2 and 0.2 mM solutions of 3 in CH2Cl2, allows us to note that, by decreasing the concentration, not only a decrease of the relative intensity is observed, but also a change in the wavelength range where this absorbance can be observed (Figure 3). Although for concentrated solutions a wide band in the range of 500–1000 nm appears at low temperature, a narrower band is observed for diluted solutions. This difference is attributed to the overlap of different absorption bands due to different species with a diverse degree of nuclearity generated at low temperature for concentrated solutions. However, for diluted conditions, a narrower distribution of nuclearities should be present in solution. This interpretation is further supported by the theoretical simulation of the optical features of the species [Pt2(S2C(CH2)5CH3)4]− (n = 1–4) (see below).
Supramolecular assembly of compounds 1, 2 and 3—effect of the ligand: The ability of compound 3 to self-assemble in solution has been compared with that of compounds 1 and 2. This comparison offers a new tool to evaluate the factors that have an effect on the aggregation of compounds of the general formula [Pt2L4]. A first difficulty that appears in this comparative study is the different solubility that each compound can offer in a common solvent such as CH2Cl2. Thus, in all cases, it is not possible to force the conditions (temperature and concentration) to maximise aggregation. In the present study the compound most reluctant to precipitate is compound 3, for which it is possible to reach a major degree of aggregation at low temperature and high concentration. However, under the same conditions, when no precipitation is observed for any of the compounds studied, compound 3 is not the one that shows a major tendency to aggregate.

The effect of the ligand can be primarily discussed regarding the results obtained in CH2Cl2. Figure 4 represents the temperature dependence of the molar absorptivity of the signal at around 700 nm that appears at low temperatures in CH2Cl2. For comparison, the data obtained for a 0.2 mm solution of [Pt2(S2CCH3)4] in CH2Cl2 previously reported are also included. Interestingly, there is an evident effect of the ligand that can be rationalised by taking into account that the steric hindrance of the ligands has not the same effect in solution than in the crystalline samples. Ordered packing minimises steric repulsive interactions especially where linear alkyl chains are present in the structure. However, free motion of such chains in solution provokes significant hindrance, which increases with the length of the alkyl group. This concept is less applicable to branched chains (as in compound 2), which present a high steric hindrance in solution that cannot be as well overcome in the ordered packing of the crystalline samples.

Supramolecular assembly of compounds 1–3 in CHCl3, THF and CS2—effect of solvent: The effect of the solvent in self-assembly of compounds 1–3 in solution has been examined by comparing the behaviour of the solutions by using CH2Cl2, CHCl3, THF and CS2 as solvent. Compounds 1–3 show comparable trends. For clarity, the discussion is centred on the results found for complex 3 (for results obtained by using complexes 1 and 2, see Figures S2 and S3 in the Supporting Information). Figure 5 shows the UV/Vis spectra of 1 mm solutions of compound 3 in the different solvents at ~50°C, which is the limit temperature that prevents precipitation in all investigated solvents. It is worth to note that the solubility in CS2 and THF is greater than in CHCl3, allowing measurements at temperatures as low as ~100°C, where some supramolecular association is observed (Figures S4–S6 in the Supporting Information). However, to compare the inherent ability of compound 3 to associate in solution in different solvents, unique conditions (such as shown in Figure 5) have to be used. Thus, under the same conditions,
whereas a certain degree of self-assembly in CH₂Cl₂ and (in less extent) in CHCl₃ is observed, CS₂ and THF hamper the association in solution. This effect could, in principle, be justified considering the known coordinative ability of such solvents, which can result in weak metal–ligand interactions between the solvent molecules and the platinum centres. In addition, solvation effects could also account for the observed trend. In any case, when the temperature is low enough, new features in the visible region appear, indicating a certain degree of self-assembly. In THF and CS₂, the new maximum absorbance appear at higher energies, which, in accordance with theoretical calculations (see below), is indicative for lower degrees of aggregation (Figures S4–S6 in the Supporting Information).

To test the conjecture that the solvent competes for coordinating [Pt₄L₄], we have performed geometry optimisations of one solvent molecule (THF and CS₂ were considered) with one [Pt₄L₄] monomer frozen at its experimental structure (see the Supporting Information for the relaxed structures). The calculations were performed by using the PBE exchange correlation functional.[14] For THF, we observed a clear attractive interaction between its oxygen atom and the Pt centre of the monomer (distance Pt–O = 3.15 Å). For CS₂, we found that only a linear configuration; that is, Pt–Pt–S–C–S, leads to a stable van der Waals complex (Pt–S = 3.52 Å), whereas the perpendicular configuration is repulsive.

Despite the lower solubility in CHCl₃, it is possible to note a greater tendency of 3 to aggregate in this solvent than in CS₂ and THF. However, CH₂Cl₂ is still the solvent that maximises the self-assembly. The near-infrared feature observed at low temperature for 1 mM solutions of compound 3 in CHCl₃ is symmetric and narrower than that observed in CH₂Cl₂ under the same conditions. Thus, CHCl₃ solutions at low temperature seem to generate a more limited number of species than that in CH₂Cl₂. Interestingly, 1 mM solutions in CHCl₃ at −50°C present a UV/Vis spectrum that is almost identical to the one observed for 0.2 mM solutions in CH₂Cl₂ at −60°C. Thus, the data obtained suggest that, in comparison with what is observed in CH₂Cl₂, in CHCl₃ compounds of the formula [Pt₄L₄] present a lower tendency to reversibly aggregate. As explained above, in this case the difference in polarity between both solvents, and thus their different ability to solvate the dimetal precursor [Pt₄L₄], is probably the fact that determines the supramolecular aggregation to form oligomers of formula [Pt₂L₄]ₜ.

Theoretical modelling: In this section, we present an elaborate study of the ground- and excited-state properties of the Pt–Pt linear chain structures by using a combination of basis sets and (time-dependent)/density functional theory (TD)/DFT methodologies.[15] We analyse the performance of different numerical approaches in the description of the electronic and optical properties of various [Pt₂L₄]ₜ clusters and offer a detailed explanation of the experimental results. To minimise calculation times, all calculations have been carried out with the representative compound [Pt₂L₄] with L = S₂CCH₃.

The crystallographic data show that [Pt₂L₄] forms stable chains in the solid phase. In solution, the formation of [Pt₂L₄]ₜ aggregates is also observed. The stability of these supramolecular entities is due to persistent weak intermolecular metal–metal interactions, which are in general difficult to describe by standard DFT methods. In addition, the presence of heavy transition-metal atoms and the large size of the system render the modelling of such structures a challenge with current theoretical approaches. According to theoretical calculations, relativistic and electronic correlation effects are thought to be important in the stability of such aggregates.

To describe accurately the energetics of [Pt₂L₄] dimerisation, our efforts demonstrate that it is necessary to use a complete basis set and to go beyond the widely used DFT methods. Thus, more sophisticated approaches are required to predict Pt–Pt bond lengths comparable with the available crystallographic experimental data. Theoretical insights on the molecular and electronic structures of [Pt₂L₄]ₜ supramolecules, as well as further analysis of the electronic transitions responsible for UV/Vis spectra are accounted below.

Properties in the electronic ground state—structure and energetics: As discussed previously, the intermolecular association process occurs through weak d···d interactions between Pt atoms. The [Pt₂L₄]ₜ structure was optimised by using different exchange-correlation DFT functionals and basis sets. The binding energies (see the Supporting Information) have been obtained from optimisations starting from a structure rearranged to facilitate the Pt–Pt contacts. Calculations were corrected for the basis set superposition error (BSSE).[16] As shown in the Supporting Information, we found that DFT performs poorly at describing accurately the energetics of this kind of interactions and yields binding energies, which are greatly scattered. For example, the widely used exchange-correlation functionals BLYP and B3LYP[17] predict a repulsive interaction between the monomers, a situation that even the long-range corrected func-

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Figure 5. UV/Vis measurements for 1 mM solutions of 3 in CH₂Cl₂, CHCl₃, CS₂ and THF at −50°C.
tional CAM-B3LYP\cite{13} is not able to correct. By using the experimental structure and the PBE\cite{14} functional in the complete basis set limit, we obtained a reasonable binding energy of \(-1.44\) \(\text{kcal mol}^{-1}\). After extensive testing, we concluded that for the purpose of the present work, which is the characterisation of the spectral properties of weakly bound metal complexes, the PBE functional family (which includes its hybrid version PBE0\cite{19}) is the best, providing a good compromise between accuracy and computing time.

Kawamura and co-workers\cite{11} reported the only experimental estimate available for the dimerisation energy of \([\text{Pt}_2(\text{S}_2\text{C}(\text{CH}_2)_5\text{CH}_3)]_2\). According to that study, the dimerisation is moderately exothermic \((\Delta H = -13 \text{ kcal mol}^{-1})\), but entropically disfavoured \((\Delta S = -0.041 \text{ kcal mol}^{-1})\). The change in the Gibbs free energy at \(-20^\circ\text{C}\) is approximately \(-2.63 \text{ kcal mol}^{-1}\). To put these numbers in context, they should be compared with the thermal energy at the same temperature \((0.50 \text{ kcal mol}^{-1})\). This comparison shows the weakness of the Pt···Pt interaction, which is favoured at sufficiently low temperatures to overcome the entropic cost of self-association.

We explored the possibility that Pt···S could lead to the formation of \([\text{Pt}_2\text{L}_4]\) supramolecular structures. In principle, one would expect some kind of attraction between Pt and S atoms of adjacent monomers. However, in our calculations, we always found that intermolecular Pt···S interaction is a repulsive one in \([\text{Pt}_2(\text{S}_2\text{C}(\text{CH}_2)_5\text{CH}_3)]_2\) and never leads to a stable structure on its own. The lack of Pt···S donor–acceptor interactions is probably due to the fact the platinum-based empty orbitals are at energies very distant from that of sulphur-based full atomic orbitals.

Geometry optimisations at distinct Pt···Pt distances were performed by taking an eclipsed disposition of the sulphur atoms between monomers as starting structure. We observed that as the monomers are brought together, a relative rotation occurs between them so as to break the eclipsed conformation of adjacent sulphur groups. This is indicative that intermolecular S···S interactions become also repulsive at the Pt···Pt equilibrium distance in \([\text{Pt}_2\text{L}_4]\). The preferred structure adopts a staggered conformation and the dihedral angle agrees well with crystallographic data (the experimental dihedral angle S-Pt···Pt-S is \(44^\circ\)). Thus, we emphasise that attractive Pt···Pt interactions are mainly responsible for the self-association of \([\text{Pt}_2\text{L}_4]\) species.

We also found a strong variation of the intramolecular Pt···Pt equilibrium distances, which are greatly scattered from 3.0 \(\text{Å}\) at the LDA level to 3.8 \(\text{Å}\) with the GGA functional (the sum of the van der Waals radii for Pt is 3.50 \(\text{Å}\)). For reasons that are still unclear, here we found that LDA (unlike GGA/hybrid functionals) seems to yield reasonable Pt···Pt intermolecular distances as already reported for aurophilic interactions\cite{20} and for Pt\textsuperscript{II} and Pt\textsuperscript{IV} pyrophosphato complexes\cite{23}. In addition, we note that the equilibrium Pt···Pt distance becomes smaller when the geometrical optimisation is performed in the presence of dichloromethane as solvent with the PCM model. Given the difficulty of reproducing the experimental geometry (in particular, the Pt···Pt interaction) with DFT, we decided to use the crystallographic structure in most of our subsequent calculations.

A differential analysis of the charge redistribution due to dimerisation of \([\text{Pt}_2\text{L}_4]\) is shown in Figure 6. The charges were computed at the PBE0 level with the LANL2TZ basis set for platinum and 6-311+G** on the rest of atoms for the crystallographic \([\text{Pt}_2\text{L}_4]\) structure and its dissociated form. Upon binding, the natural population analysis\cite{22} shows that the Pt atoms in the intermolecular region donate almost 0.05 electrons, which flow mostly to the nearby sulphur atoms, whereas the distant sulphur and methyl groups remain virtually unaffected by the dimerisation. Interestingly, this analysis highlights the leading role of the bridging ligands of the \([\text{Pt}_2\text{L}_4]\); dimetal structure in the assembly of \([\text{Pt}_2\text{L}_4]\) through Pt···Pt interactions. Specifically, NPA shows the ability of the sulphur atoms to accommodate a part of the charge donated by the platinum atoms resulting in a synergic effect in the stable linear structures. A similar behaviour is found for the Mulliken charge differential analysis (see the Supporting Information) but a more pronounced charge transfer between the atoms is observed.

The presence of dichloromethane as the solvent does not significantly change the charge differential analysis described above. The only difference is that the solvent indu-
ces a somewhat larger charge separation in the polarisable atoms such as sulphur and also the carbon atoms directly attached to them.

It is worth mentioning that, from Figure 6, there is no appreciable change in the distribution of the charge in the methyl groups of [Pt\textsubscript{2}L\textsubscript{4}] or [Pt\textsubscript{2}L\textsubscript{4}]\textsubscript{2} (and presumably of the larger linear chains). Thus, \textsuperscript{1}H NMR spectroscopy is expected to be insensitive to follow the aggregation process, as we confirmed experimentally. Moreover, a theoretical determination of the \textsuperscript{1}H chemical shift values shows no significant variation between the [Pt\textsubscript{2}L\textsubscript{4}] and [Pt\textsubscript{2}L\textsubscript{4}]\textsubscript{2} proton signals (see the Supporting Information). Undoubtedly, the \textsuperscript{195}Pt NMR technique would be better suited to monitor the self-association process between [Pt\textsubscript{2}L\textsubscript{4}] monomers than \textsuperscript{1}H NMR spectroscopy. However, our attempts to discern signals in experimental \textsuperscript{195}Pt NMR data in this system were unsuccessful, probably due to a fast chemical exchange behaviour.

As a first approach to understand the electronic description of the Pt···Pt bonding between monomer species, Figure 7 shows the energy variation of selected Kohn–Sham molecular orbitals with the Pt···Pt distance in a [Pt\textsubscript{2}L\textsubscript{4}]\textsubscript{2} system. The energies and orbitals are computed at the PBE level on a real space grid by using the OCTOPUS code\textsuperscript{[24]}. The first thing to notice is that the energy and the shape of the displayed unoccupied orbitals are practically independent of the Pt···Pt distance. Also, the HOMO–3 is unaffected because it is a MO localised exclusively in one monomer. The HOMO and HOMO–1 levels remain degenerate from 14 up to 6 Å. Further decrease of the intermonomeric distance induces an energy splitting of these MOs. Figure 7b shows that the HOMO becomes a \textit{s} antibonding combination of mainly 5d\textsubscript{z}\textsuperscript{2} (65\%) character with a significant contribution of the 6p\textsubscript{z} (4\%) and 6s (10\%) orbitals of Pt and its energy increases upon dimer formation. Conversely, the HOMO–1 is of \textit{s} bonding nature and becomes stabilised upon dimerisation.

Pure d\textsuperscript{8}···d\textsuperscript{8} interactions, that is, the combination of adjacent occupied Pt 5d\textsubscript{z}\textsuperscript{2} orbitals alone is not sufficient to explain a neat stabilisation of these supramolecular aggregates because the theoretical bond order is zero. Of course, similar association is predicted to be much stronger for d\textsuperscript{9}···d\textsuperscript{9} interactions, where the \textit{σ} bonding combination of the d\textsubscript{z}\textsuperscript{2} orbitals is occupied (HOMO) and the \textit{s} antibonding combination is unoccupied (LUMO). Thus, Pt\textsuperscript{II}···Pt\textsuperscript{II} attraction should be explained according to more subtle interactions.

The current understanding of the driving force of such weak metal–metal interaction involves a symmetry-allowed mixing between atomic orbitals of adjacent Pt atoms along the Pt–Pt vector (\textit{z} direction), namely, the occupied (donor) 5d\textsubscript{z}\textsuperscript{2} and the empty (acceptor) 6p\textsubscript{z} and 6s orbitals\textsuperscript{[25]} This overlap (we confirmed the participation of the 6p\textsubscript{z} and 6s atomic orbitals to the HOMO and HOMO–1 combinations for [Pt\textsubscript{2}L\textsubscript{4}]\textsubscript{2}, see above) strengthens the Pt–Pt interaction within each monomer and, at the same time, results in a lobe expansion of the frontier MOs that protrudes away the monomers favouring their subsequent intermolecular Pt–Pt

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**Figure 7.** a) Energy variation of selected Kohn–Sham orbitals with the distance between two monomeric [Pt\textsubscript{2}L\textsubscript{4}] species. Isosurface representation (enclosing 80\% of the charge) of these orbitals at the experimental geometry (b) and at a Pt···Pt distance of 10 Å (c). Values were calculated by using the OCTOPUS code\textsuperscript{[26]} and the PBE\textsuperscript{[14]} exchange-correlation functional.
self-association. This explanation supports the experimental evidence that short intramolecular Pt–Pt distances are also accompanied by short intermolecular Pt–Pt distances. Based on these qualitative ideas of the molecular orbital theory, Alvarez and co-workers have investigated the correlation between the pyramidalisation angle $\alpha$ (i.e., Pt–Pt–Pt–L) and the Pt–Pt distance in various dinuclear compounds including dithiocarboxylato complexes of Pt$^{II}$. To compare our calculations on [Pt$_2L_4$]$^n$ ($n = 1–4$) clusters with the results expected for an infinitely long chain ($n \to \infty$), we undertook the study of the electronic properties of the 1D periodic system at the LDA level. Figure 8 (left) displays the calculated electronic band structure along the chain direction ($x$ axis). The plot features a nearly constant LUMO level and a highly dispersive HOMO band, which becomes degenerate with the HOMO–LUMO (1) state at the edge of the first Brillouin zone (BZ). A direct band gap of 0.505 eV was calculated at the $G$ point, which is very close to the PBE value of 0.44 eV previously reported. Thus, the periodic system is predicted to be a semiconductor at this level of theory, in accordance to the aforementioned study. Our computed band gap (0.505 eV) agrees well with the extrapolated value (0.388 eV) from different HOMO–LUMO energies of the OCTOPUS calculations for [Pt$_2L_4$]$^n$ ($n = 1–4$) polymers of increasing length $n$ (fit band gap($n$) = 0.388+1.405/n eV). The difference in energy between the HOMO at the $G$ point and the edge of the BZ is 1.405 eV, which is also in good agreement with the PBE value of 1.26 eV, previously reported. In addition, we estimated the effective hole mass from a parabolic fit of the top valence band at the $G$ point. Our result (0.12, in units of the free electron mass) is, however, in contrast to the reported PBE value (0.50). Figure 8 (middle) also displays the projected density of the states (PDOS) of the periodic system and shows the important contribution of the platinum 6p and 5d atomic orbitals to the bands involved in the visible optical transitions in the periodic system.

Finally, Figure 8 (right) depicts the HOMO at selected wave vectors of the BZ of the isolated periodic chain. At the $G$ point (Figure 8, right, top), the HOMO has $\alpha$ character and features a fully antibonding combination of the platinum 5$d_{z^2}$ orbitals (with a slight involvement of the 3$p$ orbitals of the sulphur atoms) between adjacent monomers (the chain direction is now the $x$ axis). Similar findings were found in our discrete cluster calculations (Figure 7). At the edge of the BZ (Figure 8, right, bottom), however, the HOMO features an alternating pattern of bonding–antibonding $\alpha$ combination of the same orbitals, which becomes degenerated with the HOMO–LUMO$^-1$ due to the presence of two monomers within the computational cell. Due to its partial bonding character, the HOMO at the edge of the BZ is more stable than the (purely antibonding) HOMO at the $G$ point (Figure 8, left).

Excited-state properties—analysis of optical spectra: Because the HOMO in all [Pt$_2L_4$]$^n$ compounds is of $\sigma^*$ character and involves mostly Pt atoms, a complete basis set on these atoms is essential to reproduce an accurate spectrum. The basis set effect on the optical spectrum is examined in the Supporting Information. The OCTOPUS code allows us to achieve the complete basis set limit on all atoms faster than ordinary quantum chemistry codes (such as Gaussian),

Figure 8. Electronic properties of an isolated periodic chain of [Pt$_2L_4$]$^n$, computed at the LDA level. Left) Electronic band structure: dashed lines show the frontier molecular orbitals. The reduced wave vector is in units of $2\pi/L$, with $L = 11.801$ Å. The PBE band structures from reference [10b] are displayed by the red dots and agree very well with our LDA results. Middle) Projected density of states (PDOS). Right) Electronic density (enclosing a 90% of the charge) of the highest occupied molecular orbital (HOMO) at selected points in the first Brillouin zone (BZ) at the $G$ point (right, top) and at the edge of the BZ (right, bottom).
which are typically based on atom-centred basis sets. Specifically, in the case of Pt, we found that the available atom-centred basis sets (e.g., LANL2DZ and LANL2TZ) are not flexible enough. The complete basis set limit for latter methods becomes prohibitively expensive due to the size of the systems in this work. Due to the aforementioned limitations, a real-space method was chosen to study the optical absorption of [Pt\textsubscript{2}L\textsubscript{4}] systems.

As for the choice of exchange-correlation functional, previous works have shown that PBE provides a relatively good description of the optical properties of organic complexes (with some known deficiencies that are not relevant here). Moreover, in view of the reasonable predicted energetics already discussed and the correct reproduction of the experimental spectra, we decided to carry out the optics calculations with the PBE functional.

In our experimental study, we interpret the broad band at 760 nm in the UV/Vis spectra of concentrated solutions of [Pt\textsubscript{2}L\textsubscript{4}] at low temperature as an indication of the formation of oligomeric [Pt\textsubscript{2}L\textsubscript{4}] species. In order to further elucidate this assignment, we theoretically investigated the spectroscopic properties of isolated [Pt\textsubscript{2}L\textsubscript{4}]\textsubscript{+} (n = 1–4) species.

Figure 9a shows the UV/Vis spectra from real-time TD-DFT calculations at the PBE level for [Pt\textsubscript{2}L\textsubscript{4}]\textsubscript{+} (n = 1–4) computed by using the OCTOPUS code. Geometries used for these calculations were obtained from the crystalline structure without further modification. The system is assumed to be isolated in all spatial directions. The optical absorption for the three directions of polarisation for [Pt\textsubscript{2}L\textsubscript{4}]\textsubscript{+} (n = 1–4) in vacuum (Figure 9b) shows that most of the visible transitions are polarised along the axis passing through the platinum atoms.

The calculated most intense absorption peaks for the different [Pt\textsubscript{2}L\textsubscript{4}]\textsubscript{+} species are found at approximately \( \lambda = 410, 570, 686 \) and 770 nm for the series \( n = 1–4 \). These peaks correspond to neutral excitations from the HOMO (mostly a \( \sigma^* \) combination of the Pt 5d\textsubscript{z2} orbitals) to unoccupied orbitals of \( \sigma \) character involving the sulphur ligands. An isosurface representation of the most relevant orbitals in the optical transitions is given in Figure 10. In the monomer, [Pt\textsubscript{2}L\textsubscript{4}]\textsubscript{+}, the involved orbitals are from the HOMO to the LUMO +6 (63%) level. For the dimer, [Pt\textsubscript{2}L\textsubscript{4}]\textsubscript{+}, the transition involves the HOMO to the LUMO +8 (83%). In [Pt\textsubscript{2}L\textsubscript{4}]\textsubscript{+}, the contribution is more mixed but still the behaviour is the same \( \sigma^* \) to \( \sigma \). Here, the excitation from the HOMO to the LUMO +12 (34%) is the most important transition. Finally, for [Pt\textsubscript{2}L\textsubscript{4}]\textsubscript{+}, the main contribution is from the HOMO to the LUMO +16 (67%). It is worth mentioning that LDA (Perdew–Zunger parametrisation\textsuperscript{[27]}) yields similar spectra as PBE in the low energy range (see the Supporting Information).

Our calculations show that the position of the band peak in the visible region is very sensitive to the intermolecular Pt–Pt distance (see the Supporting Information). This phenomenon partially contributes to the broadening of this band when [Pt\textsubscript{2}L\textsubscript{4}] is found in solution. From Figure 7a, we can rationalise this behaviour for [Pt\textsubscript{2}L\textsubscript{4}]\textsubscript{+} due to the closing of the gap between the HOMO and the LUMO +8 levels upon decreasing the Pt–Pt distance. Interestingly, for the [Pt\textsubscript{2}L\textsubscript{4}]\textsubscript{+} dimer, the energy variation of the HOMO is responsible for this redshift, whereas the LUMO +8 is unaffected by the Pt–Pt distance.

Comparison of the broad band observed in the experimental spectrum (blue triangles in Figure 9a) with our computed spectra clearly suggests that at room temperature only monomeric [Pt\textsubscript{2}L\textsubscript{4}]\textsubscript{+} species are present, whereas at low temperature a mixture of [Pt\textsubscript{2}L\textsubscript{4}]\textsubscript{+} species with different nuclearities coexists. The observed thermochromic effect of the experimental absorption spectra of [Pt\textsubscript{2}L\textsubscript{4}]\textsubscript{+} in solution is an indication that a reversible equilibrium exists between the monomer and a mixture of various complexes of different nuclearity.\textsuperscript{1}

\textsuperscript{1} Assuming that in solution only the monomer (M) and the dimer (D) coexist, the exact expression (assuming additivity in the law of Lambert–Beer) for the average molar extinction coefficient is

\[
\varepsilon_{av} = \varepsilon_M + (\varepsilon_D - 2\varepsilon_M) \cdot \frac{M}{M + D} = \varepsilon_M \left( 1 - \frac{M}{M + D} \right) = \varepsilon_M \cdot \frac{D}{M + D}.
\]

where \( \varepsilon(\lambda) = \frac{d}{\varepsilon M} \) is the measured absorbance, \( d \) is the optical path length, \( K = \frac{M}{D} \) is the equilibrium constant of the dimerisation and \( [M] \) is the initial concentration of the monomer.
We also consider the effect of the explicit solvent (dichloromethane) on the optical spectrum of \([\text{Pt}_2\text{L}_4]_n\) and we found that the visible part of the signal remains unchanged with respect to vacuum. Only in the high-energy region we observed the dichloromethane signal as expected for this transparent solvent (see the Supporting Information).

Our results of the theoretical spectra of \([\text{Pt}_2\text{L}_4]_n\) clearly indicate that increasing the length of the oligomer results in a decrease of the energy of the optical transition associated to Pt···Pt aggregations. To take this trend to its limit, we analysed the optical properties of an isolated periodic chain of the dimer \([\text{Pt}_2\text{L}_4]_2\). The optical properties of the infinite chain were computed with the YAMBO code\(^{[28]}\) by using the LDA wavefunctions produced previously by the PWscf program\(^{[29]}\). As shown in the Supporting Information and Figure 8, for the periodic calculation we used LDA because it yields nearly the same spectra as the PBE functional. The absorption spectrum within the random-phase approximation (RPA) level is shown in Figure 11. A total of 300 bands, 17 irreducible wave vectors in the 1D first BZ, and a plane wave cut-off of 16.25 Ry were sufficient to obtain a reasonably converged spectrum. As a convergence test, the RPA spectra were also calculated with quantum espresso (QE in legend) by using a very high kinetic energy cut-off (60 Ry) to show that the main features are still well captured by the lower cut-off (16.25 Ry) of the YAMBO calculations.

As expected for 1D systems (and also found for the \([\text{Pt}_2\text{L}_4]_n\) clusters) the response in the chain direction \((x)\) is much stronger that in the perpendicular \((y, z)\) directions. The RPA spectra for light polarised in the \(x\) direction features a prominent central band with two strong peaks at \(\lambda = 400\) and 500 nm. Inclusion of local field effects (LF in the legend of Figure 11) improves the RPA spectrum significantly by shifting those peaks to higher energies as well as by reducing its intensity. Thus, the anisotropy of the system is already evident at the RPA level even though we were neglecting many body effects, which would require expensive GW/Bethe–Salpeter calculations\(^{[30]}\). LF effects were converged with 300 reciprocal lattice vectors for the dimension of the response matrix. Interestingly, we found no peak in the low-energy region of the visible spectrum (500–800 nm). However, we observed the appearance of a broad band in the near-infrared region at 1600 nm, which is consistent with a dramatic redshift due to an infinite chain of the 600 nm band found for \([\text{Pt}_2\text{L}_4]_2\). Finally, a linear response TDDFT calculation within the adiabatic LDA approximation (ALDA, in the legend of Figure 11) approximation hardly changes the LF-RPA results.
Conclusion

In this work, we demonstrate that the tendency of \([\text{Pt}_2\text{L}_4]\) to form persistent supramolecular entities can be extended to a family of compounds containing dithiocarboxylato ligands. This aggregation, which occurs through Pt–Pt interactions, can be modulated by several variables. First, high concentration and low temperatures favour the formation of \([\text{Pt}_2\text{L}_4]\). Species with different nuclearity are observed, although decreasing the initial monomer concentration results in a narrower distribution of polymeric species. Second, the supramolecular assembly of \([\text{Pt}_2\text{L}_4]\) in solution can also be tuned by the nature of the ligand \(\text{L}\). In principle, bulkier ligands inhibit the formation of oligomeric species. For example, this trend is observed in the crystal structures comparing the intermolecular Pt–Pt distances of linear versus branched ligands. Interestingly, although the length of the linear chains does not affect the intermolecular interactions in the crystal phase, it has an important impact in solution. Lastly, the solvent can also affect the supramolecular aggregation of the diplatinum complexes. Solvents containing donor atoms (such as the oxygen atom in THF or the sulphur atoms in \(\text{CS}_2\)) disfavour the aggregation by coordination to the Pt metal centre. Thus, the orbitals in the platinum centres are readily available to interact (although weakly) with the coordinating solvent molecules. However, the effect of the solvent can be more subtle as illustrated by the different results observed in \(\text{CH}_2\text{Cl}_2\) and \(\text{CHCl}_3\), where the polarity probably plays a leading role.

Theoretical simulations confirm that \([\text{Pt}_2\text{L}_4]\) species binds through weak intermolecular Pt–Pt interactions. Intermolecular Pt–S and S–S interactions between monomers have been found to be repulsive at all levels of calculations. The description of the weak Pt–Pt interaction has been particularly challenging due to issues with basis set incompleteness and limitations of current implementation of density functional theory. The description of Pt–Pt binding requires consideration of orbitals beyond the frontier ones because the HOMO is in fact of \(\sigma^*\) character, whereas the HOMO–1 is of \(\sigma\) character. This weak metal–metal attraction is mediated by the interaction between the platinum 5d\(_p\) and 6p\(_p\) atomic orbitals (the chain direction is along the \(z\) axis). In addition, the soft sulphur atoms in the dithiocarboxylato ligands assist the supramolecular assembly by accommodating the electronic charge donated by the Pt atoms involved in the Pt–Pt interaction.

From our extensive comparative study by using different methodologies, we found that a complete basis set limit is essential in order to properly describe the optical properties of these compounds. Theoretical calculations of the optical spectra allowed us to elucidate the nature of the low-energy transitions that appear at low temperature. Our calculations clearly show that the appearance of such a band is due to oligomeric species that keep their cohesion through Pt–Pt interactions. Further increasing the nuclearity of \([\text{Pt}_2\text{L}_4]\) decreases the energy of these optical transitions, the extreme case is the period isolated chain (a model of the crystal phase), which shows an absorbance, which is shifted to the infrared region. The broad band in the visible region is attributed to transitions from the HOMO, which is a \(\sigma^*\) combination of the 5d\(_p\) and the 6p\(_p\) orbital of the Pt atoms, to unoccupied molecular orbitals delocalised on the sulphur ligands.

Overall, our results lead to important advances in the understanding of how diplatinum species can assemble into 1D conductive supramolecular polymers, offering valuable hints in the search for a bottom-up assembly of molecular electronic devices.

Experimental Section

Materials and methods: All reagents were purchased from Sigma Aldrich and used as received. The solvent \(\text{CS}_2\) (purity > 99.9%) was also purchased from Sigma Aldrich and used without further purification. The synthesis of the dithiocarboxylic acids was carried out following a procedure previously reported.\(^{[10]}\) Structural characterisation of the compounds was performed by means of elemental analysis, UV/Vis and \(^1\)H NMR spectroscopy as well as single-crystal X-ray diffraction analysis. \(^1\)H NMR spectra were recorded on a Bruker AMX-300 spectrometer. C, H, S elemental analyses were performed on a Perkin–Elmer 240 B microanalyser. Electronic absorption spectra were recorded on an Agilent 8452 diode array spectrophotometer over a 190–1100 nm range in 0.1, 0.2 and 1 cm quartz cuvettes thermostatted by a Unisoku crystalliser.

Synthesis of \([\text{Pt}_2(\text{S}(_2\text{C}(_2)\text{H}_3)_2\text{CH}_2)_4]\) (1) and \([\text{Pt}_2(\text{S}(_2\text{C}(_2)\text{H}_3)_2\text{CH}_2)_4]\) (2)

The compounds were prepared following the procedure previously published by Mitsumata et al.\(^{[11]}\) The brown solid obtained upon keeping the solution 24 h at 4°C was filtered off, washed with cold -hexane and dried under vacuum. Crystals of suitable size for X-ray diffraction analysis were obtained upon slow cooling of a solution of the complex dissolved in hot dichloromethane.

Compound 1: 73% yield; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 2.78\) (t, \(J = 7.5\) Hz, 2H), 1.79–1.69 (m, 2H), 1.39–1.30 (m, 2H), 0.85 ppm (t, \(J = 7.5\) Hz, 2H); IR (KBr): \(\tilde{\nu} = 2951\) (vs), 2928 (vs), 1146 (s), 1089 cm\(^{-1}\) (vs); elemental analysis calcd (% for C\(_{20}\)H\(_{36}\)Pt\(_2\)S\(_8\)): C 26.0, H 3.9, S 27.8; found: C 25.9, H 3.8, S 27.6.

Compound 2: 71% yield; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 2.63\) (d, \(J = 7.5\) Hz, 2H), 2.13–2.14 (m, 1H), 0.90 ppm (d, \(J = 7.5\) Hz, 2H); IR (KBR): \(\tilde{\nu} = 3432\) (m), 2925 (s), 1155(s), 1003 cm\(^{-1}\) (s); elemental analysis calcd (%) for C\(_{26}\)H\(_{36}\)S\(_2\)Pt\(_2\) (923.1555): C 26.0, H 3.9, S 27.8; found: C 25.9, H 3.8, S 27.6.

Crystallographic measurements: Crystal data were collected from a cryogenic beam of \(\text{MoK}_\alpha\) radiation on a Bruker SMART 6K CCD diffractometer (for compound 1) or on an Xcalibur diffractometer (for compound 2). The structures were solved by direct methods by using the SIR92 program \(^{[39]}\) and refined by full-matrix least-squares on \(^F^2\) including all reflections (SHELXL97).\(^{[40]}\) All calculations were performed by using the WINGX crystallographic software package.\(^{[41]}\) All non-hydrogen atoms were refined anisotropically.

Crystal data for compound 1: C\(_{20}\)H\(_{36}\)Pt\(_2\)S\(_8\); \(M_r = 923.15\); T = 296(2) K; orthorhombic; space group: Pccn; \(a = 26.494(3)\), \(b = 9.1086(7)\), \(c = 11.7111(10)\) \(\text{Å}\); \(V = 2625.7(4)\) \(\text{Å}^3\); \(Z = 4\); \(\rho_{\text{calc}} = 2.170\) g cm\(^{-3}\); \(\rho_{\text{MoK}_\alpha} = 10.491\) mm\(^{-1}\); \(\rho_{\text{magn}} = 30.54^*\); 37835 reflections collected, 4318 unique reflections \((R_{\text{int}} = 0.0173)\); final \(R_1 = 0.0319\) and \(wR_2 = 0.0811\) \((I > 2\sigma(I))\); \(R_1 = 0.0402\) and \(wR_2 = 0.0893\) (all data); \(\rho_{\text{magn}} = 4.374 - 6.057\) \(\text{Å}^{-3}\).

Crystal data for compound 2: C\(_{26}\)H\(_{36}\)Pt\(_2\)S\(_8\); \(M_r = 923.15\); T = 296(2) K; orthorhombic; space group: Ccc2; \(a = 18.1699(15)\), \(b = 23.304(3)\), \(c = 20.019(3)\) \(\text{Å}\); \(V = 8476.7(18)\) \(\text{Å}^3\); \(Z = 12\); \(\rho_{\text{calc}} = 2.170\) g cm\(^{-3}\); \(\rho_{\text{MoK}_\alpha} = 10.491\) mm\(^{-1}\); \(\rho_{\text{magn}} = 26.19^*\); 15876 reflections collected, 7392 unique reflections \((R_{\text{int}} = 0.0611)\); final \(R_1 = 0.0580\) and \(wR_2 = 0.1411\) \((I > 2\sigma(I))\).
ccdc.cam.ac.uk/data_request/cif.

**Computational details:** The electronic properties of the [Pt2L4] compounds both in the ground and in the excited state were investigated by using different computational methods, most of them based on the density functional theory and its time-dependent extension (TDDFT).

In the first part, we analysed the stability of the small clusters in their ground states by using Gaussian 09 with different exchange-correlation functionals. We describe the Pt atoms with the standard double- and triple-zeta quality basis sets (LANL2DZ and LANL2TZ) with the effective core potential (ECP) approach and the 6-311+G** basis set on the other atoms. In some cases, we used the PCOM (polarisable continuum model) to study the effect of the solvent in the conformation.

A study of the change of the frontier orbitals during the dimerisation processes in the gas phase was performed by using the OCTOPUS code. With this approach, all quantities are defined on the real space by using a numerical mesh. A simulation box made with centred spheres with radii of 6.0 Å and a grid spacing of 0.18 Å. We used the PBE exchange-correlation-functional. Normal-conserving Troullier-Martins pseudopotentials were used for the non-valence electrons. The geometries were taken from our crystallographic data without further modification.

To calculate the periodic [Pt2L4] chain structure in vacuum, we used the PWscf code of the quantum espresso suite. The [Pt2L4] dimer of the experimental X-ray structure was placed with the chain axis oriented along the x direction in a 3D periodic orthorhombic box of the volume 11.801 × 29.105 × 29.105 Å3. Thus, the simulated system consists of a periodic chain of dimers in the x direction, whereas isolated in the perpendicular y,z plane. A total of 17 irreducible wave vectors was used to sample the first BZ Brillouin zone (BZ) along the chain axis (x) whereas only the Α point was sampled in the perpendicular directions (y,z). The exchange and correlation term was approximated by using the Perdew-Zunger parametrisation of the local-density-approximation (LDA).

A norm-conserving Troullier-Martins-type pseudopotential was generated for the Pt atoms, which included scalar relativistic and non-linear core corrections to describe the interaction of the core with the ten valence electrons (5d, 6s) per Pt atom. The rest of the species (C, S and H) was described with other norm-conserving pseudopotentials so that only s and p valence orbitals were explicitly considered for these elements. The Kohn-Sham valence orbitals were expanded in a plane wave basis set up to a kinetic energy cut-off of 60 Ry. The Marzari–Vanderbilt (41) smearing Kohn–Sham valence orbitals were expanded in a plane wave basis set up and p valence orbitals were explicitly considered for these elements. The corrections to describe the interaction of the core with the ten valence electrons up to the 4f level, leaving explicitly eight electrons in the semi-core (5s, 5p) and ten electrons in the valence (5d, 6s). The valence Kohn–Sham orbitals were expanded in terms of contracted Gaussian-type orbitals (GTO) of double-ζ valence-polarised (DZVP) quality for all atoms and specifically optimised for its use with the GTH pseudopotentials (DZVP–MOLOPT–GTH). A threshold of 10−6 a.u. for the energy change was adopted in the SCF wavefunction minimisation based on the direct inversion in the iterative subspace (DIIS) algorithm. The BFGS optimisation algorithm was stopped when the maximum gradient on any atom was less than 0.0001 a.u.

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