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# Unsupported $d^8$ – $d^8$ interactions in cationic $Pd^{II}$ and $Pt^{II}$ complexes: evidence for a significant metal–metal bonding character†‡

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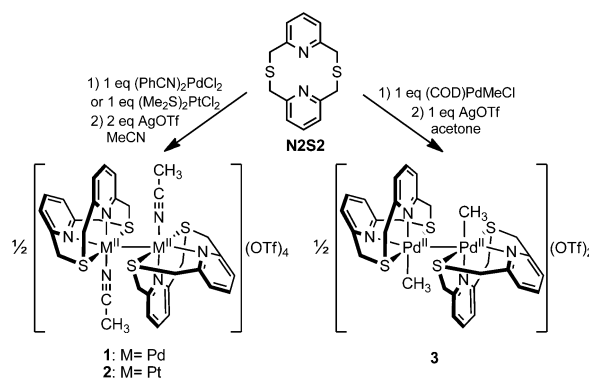
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**Isostructural dinuclear Pd and Pt complexes that exhibit unique  $d^8$ – $d^8$  interactions between dicationic metal centers are reported. These metal–metal interactions are not supported by any bridging ligands and suggest a significant metal–metal bonding character for both Pd and Pt systems.**

Numerous biological and synthetic metal-containing systems employ binuclear and multinuclear metal clusters to catalyze difficult transformations such as small molecule activation and multielectron redox reactions.<sup>1</sup> In these complexes, the presence of metal–metal interactions can play an important role in their electronic structure and reactivity.<sup>2</sup> In this context, while several  $Rh^I$ ,  $Ir^I$ , and  $Pt^{II}$  dinuclear complexes that exhibit weak  $d^8$ – $d^8$  interactions have been reported and shown to display unusual photochemical reactivity,<sup>3</sup> only a few  $Pd^{II}$  dinuclear species with metal–metal interactions have been described to date.<sup>4</sup> Reported herein are a series of  $Pd^{II}$  and  $Pt^{II}$  complexes stabilized by the tetradentate ligand 2,11-dithia[3.3](2,6)pyridinophane, N2S2, that display unique  $d^8$ – $d^8$  interactions between dicationic metal centers. Interestingly, these interactions are not supported by any bridging ligands and quantum chemical calculations suggest a significant metal–metal bonding character that is likely due to the presence of S donors and axial metal–ligand interactions. In addition, preliminary reactivity studies of a  $Pd^{II}$ -methyl complex suggest that metal–metal interactions may play a role in the methyl group transfer reactivity of such Pd complexes.

The two metal–acetonitrile complexes  $[(N2S2)Pd^{II}(MeCN)_2(OTf)_4]$  (**1**) and  $[(N2S2)Pt^{II}(MeCN)_2(OTf)_4]$  (**2**) were synthesized through the reaction of 2 equiv.  $AgOTf$  ( $OTf^- = CF_3SO_3^-$ ) with the corresponding  $(N2S2)M^{II}Cl_2$  precursors ( $M = Pd, Pt$ , Scheme 1, see ESI†).<sup>5</sup> The single crystal X-ray structures of both **1** and **2** reveal dinuclear complexes of  $C_{2h}$  symmetry in which each metal center interacts with one N2S2



Scheme 1 Synthesis of dinuclear Pd and Pt complexes.

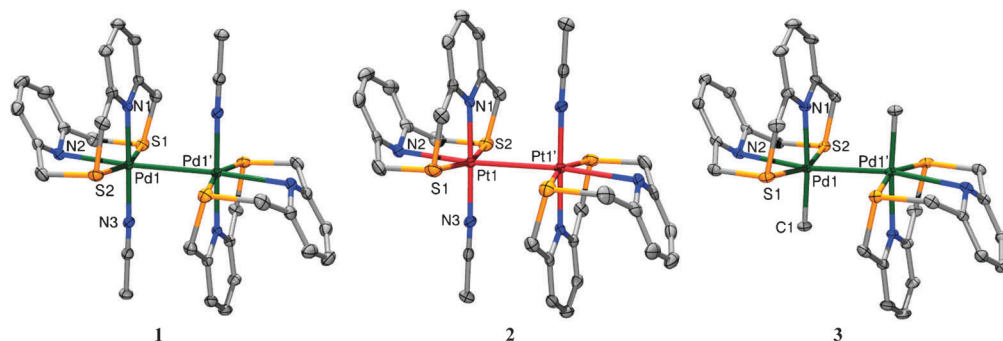
ligand and one MeCN molecule (Fig. 1).<sup>6</sup> In contrast to the symmetric conformation of N2S2 in other Pd and Pt complexes,<sup>5b</sup> N2S2 adopts an unprecedented asymmetric coordination mode in **1** and **2**: the S atoms and one pyridine N atom bind to the metal center in the equatorial plane, while the second pyridine binds weakly in the axial position. In addition, the pyridine ring is tilted *vs.* the M–N2(py) bond at an angle of 58.1° for **1** and 61.7° for **2** (Fig. 1), and the  $\pi$ – $\pi$  interaction between the two pyridine rings of one N2S2 ligand likely favors the observed ligand conformation.<sup>7</sup> Interestingly, the distorted octahedral geometry of the Pd and Pt centers is completed by a metal–metal interaction. The  $Pd^{II}\cdots Pd^{II}$  distance of 3.066 Å in **1** and the  $Pt^{II}\cdots Pt^{II}$  distance of 3.077 Å in **2** are significantly less than the sum of the van der Waals radii for Pd (3.26 Å) and Pt (3.50 Å), respectively,<sup>8</sup> consistent with the previously reported  $d^8$ – $d^8$  interactions ranging from 2.55 to 3.35 Å.<sup>3,4</sup> Notably, complexes **1** and **2** represent to the best of our knowledge the first examples of  $d^8$ – $d^8$  interactions between two dicationic metal fragments. However, the  $Pd\cdots Pd$  distance in **1** is similar to those in some other Pd dinuclear complexes containing neutral metal centers,<sup>4b–d,g,h</sup> suggesting that the metal–metal interaction overcomes the coulombic repulsion between the two dicationic metal centers. Moreover, the  $d^8$ – $d^8$  interaction in **1** (and **2**) is not supported by any bridging ligand, in contrast to almost<sup>9</sup> all other dinuclear  $Pd^{II}$  complexes in which the metal–metal interactions are stabilized by either bridging ligands<sup>4a,c–h</sup> or dinucleating ligands.<sup>4g</sup> Overall, both the presence of  $d^8$ – $d^8$  interactions between two dicationic metal centers and the absence of a

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‡ Electronic supplementary information (ESI) available: Experimental and computational details, X-ray crystallographic data, spectroscopic characterization, and reactivity studies. CCDC 842462 (**1**), 842463 (**2**) and 842464 (**3**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc15420f

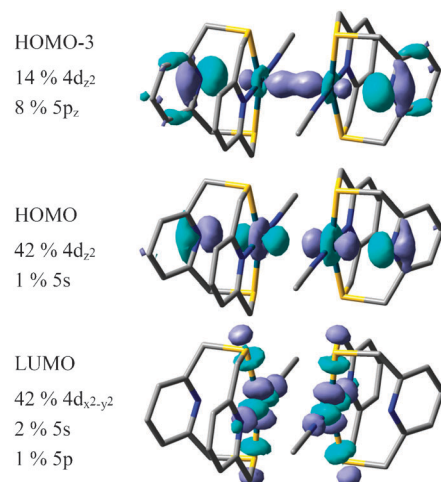


**Fig. 1** X-Ray crystal structures of **1**, **2**, and **3** with 50% thermal ellipsoids. Selected bond distances (Å): **1**: Pd1–S1 2.3275(5), Pd1–S2 2.3230(5), Pd1–N1 2.000(1), Pd1–N2 2.505(2), Pd1–N3 2.015(2), Pd1⋯Pd1' 3.0657(3); **2**: Pt1–S1 2.316(1), Pt1–S2 2.319(1), Pt1–N1 2.005(3), Pt1–N2 2.584(3), Pt1–N3 1.995(3), Pt1⋯Pt1' 3.0768(3); **3**: Pd1–S1 2.3447(3), Pd1–S2 2.3370(2), Pd1–N1 2.1049(6), Pd1–N2 2.5739(7), Pd1–C1 2.0389(8), Pd1⋯Pd1' 3.1132(2).

bridging ligand in **1** and **2** strongly suggest the presence of a significant metal–metal bonding character.

Variable temperature (VT)  $^1\text{H}$  NMR measurements in  $\text{CD}_3\text{CN}$  reveal that **1** and **2** exhibit a symmetric structure at room temperature due to fast ligand rearrangement,<sup>10</sup> suggesting the formation of a monomeric Pd species in solution.<sup>11</sup> No change in the NMR spectrum of **1** was observed at lower temperatures, while for **2** a coalescence of the signals is observed at  $\sim -40$  °C, suggesting an asymmetric coordination mode (see ESI†). The observed difference between **1** and **2** is likely due to the increased lability of Pd vs. Pt.<sup>10</sup> However, ESI-MS studies reveal the presence of dinuclear species in solution for both **1** and **2**, suggesting that the metal–metal interactions can persist to some extent in coordinating solvents such as MeCN (see ESI†).<sup>12</sup>

The formation of an unsupported  $d^8$ – $d^8$  metal–metal interaction between two dicationic metal fragments is unique. In general, such  $d^8$ – $d^8$  weakly bonding interactions have been explained by the symmetry allowed mixing of the metal  $(n + 1)$   $p_z$  and  $s$  orbitals into the  $d_{z^2}$  orbitals of the two interacting metals,<sup>3a,4f</sup> the extent of orbital mixing being greater for  $\text{Pt}^{\text{II}}$  than  $\text{Pd}^{\text{II}}$ .<sup>4h</sup> The metal–metal interactions in **1** and **2** were investigated through DFT calculations that reveal the typical  $d_{z^2}$   $\sigma^*$  metal–metal antibonding and  $\sigma$  bonding HOMOs for both **1** and **2**,<sup>3a,4f</sup> while the LUMOs are  $d_{x^2-y^2}$  metal–ligand antibonding orbitals that can be involved in a weak  $\delta$ -type metal–metal bonding interaction (Fig. 2 and Tables S3 and S5, ESI†).<sup>4f,h,13</sup> Such LUMOs with weakly  $\delta$  metal–metal interactions have been also reported for Pt dinuclear complexes with significant metal–metal bonding character.<sup>14</sup> In addition, the calculated  $(n + 1)$   $p_z$  contributions to the molecular orbitals of **1** and **2** are similar for both Pd and Pt complexes and comparable to those in other Pd dimers,<sup>4f,h</sup> providing further evidence for the metal–metal bonding character (Fig. 2, see ESI†). We propose that the enhanced metal–metal bonding in **1** and **2** is due to the more covalent metal–S interactions, which lead to: (a) a higher energy of the metal-based antibonding orbitals, which in turn can mix to a greater extent with the  $(n + 1)$  metal  $p_z$  and  $s$  orbitals, and (b) an increased energy of the  $\delta$  metal–metal bonding orbital that becomes the LUMO. The calculated Pd–Pd bond order of 0.19 for **1** and the Pt–Pt bond order of 0.24 for **2** provide additional support for this hypothesis.<sup>4f,h</sup> Moreover, the unique interactions



**Fig. 2** Selected molecular orbitals of **1**, with percentage contribution from Pd atomic orbitals (balance from ligand-based orbitals).

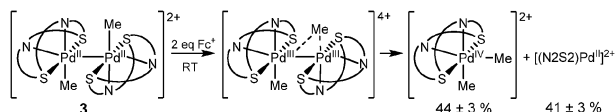
of the metal centers with the axial pyridine rings in **1** and **2** are proposed to further enhance the metal–metal interactions by raising the energy of the metal  $d_{z^2}$  orbitals (Fig. 2 and Tables S3 and S5, ESI†).<sup>15</sup>

The UV-vis absorption spectra of **1** and **2** were recorded in both the solid state and in solution (Table 1). The solid state spectra reveal low energy transitions at 425, 567, and 683 nm for **1** and 465, 545, and 675 nm for **2** (see ESI†). Based on time-dependent DFT calculations and previous studies,<sup>14</sup> we tentatively assign the bands in **1** to  $\sigma^*[d_{z^2}(\text{Pd}_2)] \rightarrow \pi^*[(\text{ligand})]$ ,  $\sigma^*[d_{z^2}(\text{Pd}_2)] \rightarrow \delta[d_{x^2-y^2}(\text{Pd}_2)]/\sigma^*(\text{Pd-S})$ , and  $\sigma[d_{z^2}(\text{Pd}_2)] \rightarrow \delta^*[d_{x^2-y^2}(\text{Pd}_2)]/\sigma^*(\text{Pd-S})$  metal–metal to ligand charge transfer (MMLCT) transitions, respectively; similar band assignments are proposed for **2** (see ESI†).<sup>4f</sup> Upon dissolution of **1** and **2**, their UV-vis spectra reveal the disappearance of the low-energy transitions (Table 1), likely due to the dissociation of the

**Table 1** UV-vis absorption data for **1**, **2**, and **3**

Compound	$\lambda_{\text{max}}^a/\text{nm}$	$\lambda_{\text{max}}/\text{nm}$ ( $\epsilon/\text{cm}^{-1} \text{M}^{-1}$ ) <sup>b</sup>
<b>1</b>	425, 567, 683	244 (28000), 342 (8100), 515 (800)
<b>2</b>	465, 546, 675	260 (22000), 356 (3000), 404 (1300)
<b>3</b>	545, 688	289 (4600), 346 (1400)

<sup>a</sup> In the solid state. <sup>b</sup> In MeCN.



**Scheme 2** Reaction of **3** with 2 equiv.  $\text{Fc}^+$  in acetone- $d_6$ .

dinuclear species.<sup>16</sup> Interestingly, the absorption bands of **1** and **2** occur at lower energies than those of other  $\text{Pd}^{\text{II}}\text{-Pd}^{\text{II}}$  complexes<sup>4</sup> and thus are not overlapping with ligand-based transitions.<sup>4f,g,17</sup>

In light of our interest in the chemistry of high-valent Pd systems,<sup>18</sup> we began to investigate the oxidative reactivity of organometallic (N2S2)Pd complexes. Interestingly, when the (N2S2)Pd<sup>II</sup>MeCl complex is reacted with 1 equiv. AgOTf, the isolated product is a dinuclear Pd complex [(N2S2)Pd<sup>II</sup>Me]<sub>2</sub>(OTf)<sub>2</sub> (**3**) that exhibits a solid-state structure and Pd–Pd interaction similar to **1** (Fig. 1),<sup>19</sup> as confirmed by solid-state UV-vis, ESI-MS, and VT NMR studies (Table 1, see ESI†). Oxidation of **3** with 2 equiv. ferrocenium hexafluorophosphate ( $\text{Fc}^+$ ) in acetone- $d_6$  at 25 °C leads to formation of a surprisingly stable Pd<sup>IV</sup> species [(N2S2)Pd<sup>IV</sup>Me]<sub>2</sub><sup>2+</sup> in 44% yield and an equivalent amount of a [(N2S2)Pd<sup>IV</sup>]<sub>2</sub><sup>2+</sup> species (see ESI†). Since it is well established that oxidation of d<sup>8</sup>–d<sup>8</sup> complexes forms d<sup>7</sup>–d<sup>7</sup> systems with enhanced metal–metal bonding,<sup>3b,20</sup> we propose that oxidation of **3** generates a Pd<sup>III</sup>–Pd<sup>III</sup> species with a shorter Pd–Pd bond that promotes the observed methyl group transfer and disproportionation reaction (Scheme 2).<sup>21</sup>

In summary, the Pd<sup>II</sup> and Pt<sup>II</sup> complexes described herein display unique d<sup>8</sup>–d<sup>8</sup> interactions between dicationic metal fragments that are not supported by any bridging ligands, strongly suggesting the existence of a significant metal–metal bonding character. In addition, preliminary reactivity studies suggest that such metal–metal interactions may be involved in methyl group transfer reactions. Current research efforts are aimed at probing the role of such interactions in other organometallic reactions.

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- Unfortunately, the tetracationic complexes **1** and **2** are not soluble in noncoordinating solvents such as CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub>, while their solubility in MeCN may be due to complex dissociation.
- Based on the classification by Hazari, Doyle, *et al.* (ref. 4h), complexes **1** and **2** belong to class (ii) of d<sup>8</sup>–d<sup>8</sup> dinuclear complexes, as the excitation of an electron into the LUMO leads to an increase in the metal–metal bond order of 0.5.
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