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# Chelating and Bridging Roles of 2-(2-Pyridyl)benzimidazole and Bis(diphenylphosphino)acetylene in Stabilizing a Cyclic Tetranuclear Platinum(II) Complex

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S Supporting Information

**ABSTRACT:** The reaction of complex [Pt(Me)(DMSO)(pbz)], 1, (pbz = 2-(2-pyridyl)benzimidazolate) with  $[PtMe(Cl)(DMSO)_2]$ , B, followed by addition of bis(diphenylphosphino)acetylene (dppac), gave the novel tetranuclear platinum complex [ $Pt_4Me_4(\mu$ dppac)<sub>2</sub>(pbz)<sub>2</sub>Cl<sub>2</sub>], 2, bearing both the pbz and dppac ligands. In this structure, the pbz ligands are both chelating and bridging to stabilize the tetraplatinum framework. The tetranuclear Pt(II)complex was fully characterized by NMR spectroscopy, X-ray crystallography, and mass spectrometry, and its electronic structure was investigated and supported by DFT calculations.



# INTRODUCTION

The construction of multinuclear metal assemblies has been a growing area of research during the past decade.<sup>1,2</sup> Developments based on the use of different ligands as the building unit for the synthesis of compounds have been reported for binuclear Pt complexes,<sup>3-6</sup> although to the best of our knowledge, tetranuclear complexes are rare.<sup>7-9</sup>

Wilson and Lippard reported<sup>10</sup> a tetranuclear platinum complex in which two acetate-bridged diplatinum(III) units are connected by two bridging amido ligands (I, Chart 1). The syntheses of tetranuclear platinum complexes in which the metal centers are supported by phosphido ligands have been reported by Forniés and co-workers (II, Chart 1).<sup>11</sup> Stang and Cao reported<sup>12</sup> the preparation and characterization, via selfassembly, of platinum- and palladium-based cationic, tetranuclear, macrocyclic complexes (III, Chart 1). In these complexes, 4,4'-bipyridine acts as a spacer ligand between the Pt centers. Youngs and co-workers also reported<sup>13</sup> the synthesis of tetraplatinum square heterocycle which had large cavities and in which the rings were composed of only platinum and butadiyne fragments (IV, Chart 1). They used chelating phosphines in order to enforce the required cis geometry at the platinum atom. Yam et al.<sup>14</sup> synthesized a Vshape luminescent tetranuclear platinum(II) alkynyl complex (V, Chart 1), and its electrochemical behavior was studied by cyclic voltammetry. More recently, a tetranuclear Pt(II)

compound using 1,2,3-tetrazolate as a building block (VI, Chart 1) was reported<sup>15</sup> in which all triazolate nitrogen atoms are coordinated to 3 different Pt(II) ions. Casas and coworkers synthesized<sup>16</sup> a tetranuclear platinum(II)-platinum-(IV) mixed-valence complexes by addition of a stoichiometric amount of a Pt(II) reagent  $[cis-[Pt(C_6F_5)_2(thf)_2]$  to some binuclear platinum(IV) complexes (VII, Chart 1).

Cyclometalated complexes have attracted attention because of their several applications in science.<sup>17-21</sup> Of particular interest are cycloplatinated complexes bearing strong field ligands such as benzo[h]quinolinate (bhq) and 2-phenylpyridinate (ppy) (VIII, Chart 1).<sup>22-27</sup> The cycloplatinated(II) compounds with the  $[Pt(C^N)R]$  moiety  $(C^N=cyclo$ metalated ligand and R= alkyl, aryl or halide) are very attractive due to their ease of preparation through C–H activation of ligands like 2-phenylpyridine (Hppy) and benzo[h]quinoline (Hbhq) (VIII, Chart 1) with a suitable Pt(II) precursor complex.<sup>24-33</sup> Earlier, we have studied the reaction of the double rollover cycloplatinated(II) complex  $[Pt_2(\mu-bpy-2H)(Me)_2(\kappa^1-dppm)_2]$ , bpy= 2,2'-bipyridine (in which each metallic center bears a monodentate dppm ligand) with the known monomeric cycloplatinated (II) complex  $[Pt(Me)(bhq)(SMe_2)]$  in a 1:2 molar ratio. This reaction

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### Chart 1. Examples of Some Tetraplatinum Complexes



resulted in the unsymmetrical tetranuclear complex [{(bhq)-(Me)Pt( $\mu$ -dppm)Pt(Me)}<sub>2</sub>( $\mu$ -bpy-2H)] (IX, Chart 1).<sup>29</sup>

The 2-(2-pyridyl)benzimidazole (Hpbz) ligand normally acts as an anionic N<sup> $\Lambda$ </sup>N bidentate ligand through N–H bond activation of the imidazole unit (instead of C–H activation in Hppy and Hbhq ligands).<sup>34–38</sup> Hpbz derivatives have been used as "bipyridine analogues" in some complexes with metal centers such as Cu(I, II),<sup>39</sup> Zn(II),<sup>40</sup> Ru(II),<sup>41</sup> Os(II),<sup>42</sup> and Re(I).<sup>43,44</sup> The ease of synthesis and the commercial availability of Hpbz make it an attractive ligand. Although there are many reports on preparation of metal complexes in which pbz acts as a N<sup> $\Lambda$ </sup>N bidentate ligand, complexes bearing this ligand as a bridging ligand between two metal centers have not been studied until now.

Reactions of biphosphine ligands to form polynuclear complexes with metal centers supported by these bridging ligands have produced rich and interesting chemistry.<sup>30,45–49</sup> However, to the best of our knowledge, there are no reported complexes where 2-(2-pyridyl)benzimidazole acts concurrently as a chelating and bridging ligand. This, together with our interest in the design and synthesis of organoplatinum(II) complexes,<sup>50–58</sup> prompted us to exploit the 2-(2-pyridyl)-benzimidazole and bis(diphenylphosphino)acetylene (dppac) units as the backbone for the construction of a cyclic tetraplatinum(II) complex. Here we report an interesting tetranuclear organoplatinum(II) complex in which, for the first time, the pbz anion acts as both a chelating and a bridging ligand to stabilize the tetraplatinum framework. In this

complex, dppac also serves as a bridging ligand. The electronic structure of this complex, supported by theoretical calculations, is also investigated.

#### EXPERIMENTAL SECTION

**General Remarks.** The <sup>1</sup>H and <sup>31</sup>P NMR spectra were recorded on a Bruker Avance DPX 400 MHz spectrometer using TMS (<sup>1</sup>H) and  $H_3PO_4$  (<sup>31</sup>P) as references. CDCl<sub>3</sub> was used as solvent for NMR spectroscopy. All chemical shifts and coupling constants are reported in ppm and Hz, respectively. Microanalyses were done using a Thermo Finnigan Flash EA-1112 CHNSO rapid elemental analyzer, and melting points were measured on a Buchi 530 instrument. UV– vis absorption spectra were recorded on a PerkinElmer Lambda 25 spectrophotometer using a cuvette with 1.00 cm path length. The complexes [Pt(Me)<sub>2</sub>(DMSO)<sub>2</sub>], A,<sup>59</sup> and [Pt(Me)(DMSO)(pbz)], 1,<sup>60</sup> were synthesized by known methods. Bis(diphenylphosphino)acetylene (dppac) and 2-(2-pyridyl)benzimidazole (Hpbz) were purchased from commercial sources.

**Synthesis of Pt Complexes.** [*Pt(Me)Cl(DMSO)*<sub>2</sub>], **B**. This compound had been previously synthesized by the reaction of [PtCl<sub>2</sub>(DMSO)<sub>2</sub>] with SnMe<sub>4</sub> for 24 h with a yield of 55%.<sup>61</sup> In an alternative method, 381 mg (1.00 mmol) of **A** and 421 mg (1.00 mmol) of [PtCl<sub>2</sub>(DMSO)<sub>2</sub>] were added to 50 mL of chloroform or acetone and stirred for 6 h. The solvent was then removed by evaporation to give 640 mg of compound **B** (1.59 mmol). Yield: 80%. <sup>1</sup>H NMR in CDCl<sub>3</sub>: *trans* isomer:  $\delta$  0.99 [s, <sup>2</sup>J<sub>PtH</sub> = 78.9 Hz, 3H, Me]; 3.42, [s, <sup>3</sup>J<sub>PtH</sub> = 24.2 Hz, 12H, Me of DMSO]; *cis* isomer:  $\delta$  1.17 [s, <sup>2</sup>J<sub>PtH</sub> = 79.0 Hz, 3H, Me]; 3.21, [s, <sup>3</sup>J<sub>PtH</sub> = 8.8 Hz, 6H, DMSO *trans* to Me]; 3.49 [s, <sup>3</sup>J<sub>PtH</sub> = 38.2 Hz, 6H, DMSO *trans* to Cl].

[*Pt*<sub>4</sub>(*Me*)<sub>4</sub>(*μ*-*dppac*)<sub>2</sub>(*pbz*)<sub>2</sub>*Cl*<sub>2</sub>], **2**. [Pt(Me)Cl(DMSO)<sub>2</sub>], **B**, (401 mg, 1.00 mmol) was added to a solution of **1** (482 mg, 1.00 mmol) in acetone (100 mL). This was stirred at room temperature for 24 h, and then dppac (394 mg, 1.00 mmol) was added to the solution. After 20 h, the solvent was removed, and the yellow residue was washed with cold diethyl ether to give 800 mg of **2** (0.381 mmol). Yield: 76%. Mp > 250 °C. Anal. Calcd for C<sub>80</sub>H<sub>68</sub>Cl<sub>2</sub>N<sub>6</sub>Pt<sub>4</sub>P<sub>4</sub>: C, 46.0; H, 3.2; N, 4.0%. Found, C, 45.8; H, 3.4; N, 4.1%. NMR in CDCl<sub>3</sub>: δ(<sup>1</sup>H) 0.56 [d, <sup>2</sup>J<sub>PtH</sub> = 83.5 Hz, <sup>3</sup>J<sub>PH</sub> = 7.3 Hz, 6H, Me ligands *trans* to N of 2-pyridyl ring], 1.09 [d, <sup>2</sup>J<sub>PtH</sub> = 72.6 Hz, <sup>3</sup>J<sub>PH</sub> = 4.7 Hz, 6H, Me ligands *trans* to N of benzimidazole ring]; 8.15 [dd, <sup>3</sup>J<sub>PtH</sub> = 43.6 Hz, <sup>3</sup>J<sub>HH</sub> = 6.5 Hz, <sup>4</sup>J<sub>PH</sub> = 5.3 Hz, 2H, H<sup>6</sup>]; 7.84 and 7.33 [m, Ph of dppac]; 7.45 [m, H<sup>6'</sup> and H<sup>3'</sup>]; 6.90 [d, <sup>3</sup>J<sub>HH</sub> = 5.4 Hz, 2H, H<sup>3</sup>]; 6.79 [t, <sup>3</sup>J<sub>HH</sub> = 15.1 Hz, 2H, H<sup>4'</sup>]; 6.07 [d, <sup>3</sup>J<sub>(HH)</sub> = 8.6 Hz, 2H, H<sup>4</sup>]. δ(<sup>31</sup>P) 27.9 [s, <sup>1</sup>J<sub>PtP</sub> = 2545 Hz, 2P, *trans* to benzimidazole ring], 20.6 [s, <sup>1</sup>J<sub>PtP</sub> = 4392 Hz, 2P, *trans* to Cl]. ESI-TOF-MS: *m*/z 2107.4 [**2** + H<sub>3</sub>O]<sup>+</sup>, 1717.4 [**2** - dppac + Na]<sup>+</sup> (Chart 2).

#### Chart 2. NMR Labeling for Complex 2



**Crystallographic Data.** The structure of complex **2** was determined from single-crystal X-ray diffraction data at 100(2) on a Bruker KAPPA APEX II diffractometer equipped with an APEX II CCD detector using a TRIUMPH monochromator with a Mo K $\alpha$  X-ray source (k = 0.71073 Å). The crystal was mounted on a cryoloop under Paratone-N oil and kept under nitrogen. The SADABS<sup>62</sup> method is used for absorption correction of the data, and the SHELXTL<sup>63</sup> software is used for subsequent calculations, structure

solution, refinement, and creation of publication data. Structure determination was carried out using intrinsic methods. Crystallographic information is reported in Table 1. Crystallographic data is

Гable	1.	Crystal	and	Structure	Refinement	for	Complex	2•
4(CH <sub>2</sub>	),	CO					_	

empirical formula	$C_{92}H_{92}Cl_2N_6O_4P_4Pt_4$
formula weight	2320.85
temperature (K)	100(2)
wavelength (Å)	0.71073
crystal system	triclinic
space group	$P\overline{1}$
a/Å	11.207(3)
b/Å	11.658(3)
c/Å	17.085(5)
$\beta/^{\circ}$	94.774(7)
volume/Å <sup>3</sup>	2151.6(10)
Ζ	1
density (calculated)/(mg/m <sup>3</sup> )	1.791
absorption coefficient/mm <sup>-1</sup>	6.672
F(000)	1124
theta range for data collection	1.229-27.266°
reflections collected	18876
independent reflections, [R(int)]	9565, [0.0356]
max. and min transmission	0.7455 and 0.5607
data/restraints/parameters	9565/0/511
goodness-of-fit on $F^2$	0.976
$R_1/wR_2 \left[I > 2\sigma(I)\right]$	0.0294/0.0596

deposited with the Cambridge Crystallographic Data Centre, No. CCDC 1874226. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: + 44(1223)336–033, e-mail: deposit@ccdc.cam.ac.uk, or www.ccdc.cam.ac.uk.

**Computational Details.** Gaussian 09 was used<sup>64</sup> to fully optimize the structure at the B3LYP level of density functional theory (DFT). The effective core potential of Hay and Wadt with LANL2DZ was selected for  $Pt^{65}$  and the 6-31G(d) basis set was chosen for all other atoms. To estimate and confirm the optimized structures of the molecules, frequency calculations were carried out to obtain only real frequencies for the optimized structures. The calculations for the electronic absorption spectra using time-dependent DFT (TD-DFT) were done at the same level of theory (B3LYP). The "Chemissian" software<sup>66</sup> is used to show the compositions of molecular orbitals and also to plot the theoretical absorption spectra.

#### RESULTS AND DISCUSSION

**Complex Synthesis and Characterization.** The detailed synthetic route for the tetranuclear complex  $[Pt_4(Me)_4(\mu-dppac)_2(pbz)_2Cl_2]$ , **2**, is depicted in Scheme 1. The precursor complex [Pt(Me)(DMSO)(pbz)], **1**, was prepared through the reaction of  $[Pt(Me)_2(DMSO)_2]$ , **A**, with Hpbz in 1:1 ratio. In the key step, complex **B** was added to a solution of **1** in acetone to produce an intermediate which is suggested to be the dimeric Pt complex  $[Cl(Me)(DMSO)Pt(\mu-pbz)Pt(Me)-(DMSO)]$ , **C**. Then, dppac was added in situ to the solution to result in the assembly of **2** (in 76% yield) as a yellow solid.

The structure of new complex **2** was fully characterized using multinuclear NMR spectroscopy (<sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR), electrospray ionization mass spectroscopy (ESI-MS), and single-crystal X-ray crystallography. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum is illustrated in Figure 1A (details of the NMR spectra are provided in the Experimental Section). The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **2** displays two distinct singlets

## Scheme 1. Route to Preparation of Complex 2



Figure 1. (A) <sup>31</sup>P and (B) <sup>1</sup>H (aliphatic region) NMR spectra of complex 2.

with equal intensities, having platinum satellites. They appear at  $\delta = 20.6 ({}^{1}J_{PtP} = 4392 \text{ Hz})$  and 27.9 ( ${}^{1}J_{PtP} = 2545 \text{ Hz})$ , which are respectively assigned to the P trans to Cl and the P trans to ligating N atom of benzimidazole ring, in agreement with the higher trans influence of N compared to Cl. It should be noted that the  ${}^{1}J_{PtP}$  values of 4264 and 3081 Hz were previously reported for the P atom trans to Cl in complexes [Pt(Me)(dppe)Cl] (dppe =  $Ph_2PCH_2CH_2PPh_2$ ) and  $[PtCl_2(dppm)]$  (dppm =  $Ph_2PCH_2PPh_2$ ),<sup>67</sup> respectively. On the basis of the <sup>1</sup>H NMR spectrum of 2 (see Figure 1B), two different Me groups are observed, being trans to pyridyl and benzimidazole rings. The Me group trans to ligating N of pyridyl was observed at  $\delta = 0.56$  as a doublet with  ${}^{2}J_{\text{PtH}} = 83.5$ Hz and  ${}^{3}J_{PH}$  = 7.3 Hz, while the Me group trans to the ligating N of benzimidazole ring appeared at  $\delta$  = 1.09 ppm with a considerably lower  ${}^{2}J_{PtH} = 72.6$  Hz and  ${}^{3}J_{PH} = 4.7$  Hz values. This observation indicates a stronger trans influence of the ligating N of benzimidazole ring in comparison to the 2-pyridyl ring.

**Crystal Structure.** Yellow crystals of complex **2** were obtained upon diffusion of *n*-hexane vapor into the acetone solution. The structure obtained by X-ray crystallography

technique is presented in Figure 2, and the numerical data summarized in Table 1 (see the caption of Figure 2 for selected geometrical parameters). To our knowledge, complex 2 is the first example of a tetranuclear Pt complex having both bridging 2-(2'-pyridyl)benzimidazolate and bis(diphenylphosphino)acetylene ligands. In this structure, pbz ligands act as both chelating and bridging ligand to stabilize the tetraplatinum framework. The molecular structure of complex 2 confirms the  $Pt_4(dppac)_2(pbz)_2$  framework. As shown in Figure 2, the solid state structure exhibits distorted four-coordinated square planar geometry around the platinum centers. The methyl groups are trans to the pyridyl and benzimidazole rings of pbz ligand. The largest deviation from ideal square planar geometry belongs to the N3-Pt2-N2 angle at 78.01(13)° which is associated with the Pt(pbz) chelate ring. One of the P atoms of dppac is located trans to the ligating N of benzimidazole ring (Pt2-P2 = 2.1910(13) Å) and another one is trans to the Cl atom (Pt1-P1 = 2.1754(12) Å). The Me groups are located trans to the ligating N of the pyridyl (Pt2–C26 = 2.054(4) Å) and benzimidazole (Pt1-N1 = 2.122(3) Å) rings (See Figure 2). Therefore, the structure of complex 2 confirms that "Pt( $\mu$ pbz)Pt" moieties are connected through dppac bridging ligand



Figure 2. (top) Structure of complex 2. All hydrogen atoms and solvent molecules are omitted for clarity. Selected geometrical parameters (Å, deg): Pt1–Cl1 2.3597(12); Pt1–Cl 2.064(4); Pt1–P1 2.1754(12); Pt1–N1 2.122(3); Pt2–N2 2.078(4); Pt2–N3 2.134(3); Pt2–P2 2.1910(13); Pt2–C26 2.054(4); Cl1–Pt1–N1 88.28(10); Cl1–Pt1–P1 175.11(4); Cl1–Pt1–Cl 86.89(12); N1–Pt1–P1 96.52(10); P2–Pt2–N3 104.73(10); P2–Pt2–C26 83.69(13); N3–Pt2–N2 78.01(13); N2–Pt2–C26 93.63(16). (bottom) 18-membered  $Pt_4P_4N_4C_6$  central core of tetranuclear complex 2.

in which the P–C–C–P fragment is almost linear. The terminal Me ligands are trans in relation to each other. It should be noted that this kind of bridged dppac complex where a dppac molecule acts as a bridging ligand between two metal fragments is not common.<sup>3,67,68</sup>

ESI-MS result further confirms the molecular formulas formation by demonstrated isotopically well-resolved peak at m/z = 2107.4 which is related to  $[2 + H_3O]^+$ . The peak matched well with its calculated theoretical isotope distributions (see Figure 3).

Absorption Spectrum. Complex 2 is stable in most common organic solvents including acetone, CH2Cl2, CHCl3, and CH<sub>3</sub>CN, which allows the investigation of its absorption spectrum in a wide range of solvents. Figure 4A shows the absorption spectrum of 2 in several common organic solvents, and it is notable that the maxima of the two intense bands in the 300-400 nm region are essentially independent the solvent, occurring, for example, at 312 and 358 nm in CH<sub>2</sub>Cl<sub>2</sub> ( $\varepsilon = 3.00 \times 10^4$  and  $2.60 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup>, respectively). In order to gain further insight into the nature of electronic transitions, TD-DFT calculations were performed on the optimized ground state geometries. As shown in Figure 4B, the computed absorption spectrum (bars) is in good agreement with its experimental spectrum. The numerical data for the selected calculated wavelengths together with their assignments are listed in Table 2, while plots of key molecular orbitals are shown in Figure 5. The lower energy absorption band is concluded to be an admixture of ligand (L' = Cl) to ligand (L = pbz) charge transfer (L'LCT) and metal (Pt) to L charge transfer (MLCT) transitions, while the higher energy



**Figure 3.** Expanded (left) and simulated (right) isotopic pattern ESI-MS spectrum of complex  $[2 + H_3O]^+$ , showing the expected intensity due to isotopic distribution. The small differences between simulation and experimental patterns may be related to small impurities of carrier-solvent used for the experiment.



Figure 4. (A) UV–visible absorption spectrum of complex 2 at different solvents  $(1.0 \times 10^{-5} \text{ M})$ ; dashed line shows the UV–visible spectrum of acetone, UV cutoff of acetone is 330 nm. (B) Overlaid experimental absorbance (spectrum) and calculated TD-DFT (bar) for complex 2 in CH<sub>2</sub>Cl<sub>2</sub>.

band is attributed to an admixture of L'LCT, MLCT and intraligand (IL) transitions.

In addition to the contours and energies of several highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) for the ground-state structure of the tetranuclear platinum complex **2**, Figure 5 also lists the corresponding partial MO compositions (percentages). The calculated HOMO–LUMO energy gap is 3.588 eV. Analysis of the frontier molecular orbitals reveals that the maximum contributions to HOMO and HOMO–1 belong to the choride ligand and Pt metal center (in PtMeCINP moiety) with a small

Table 2. TD-DFT Computed	Spectrum at the Gro	ound State Geometr	ry of 2 Compared to t	the Experimental Spectrum	in
$CH_2Cl_2$ Solution 1 × 10 <sup>-5</sup> M	a				

$\lambda_{\mathrm{cal}}(f)^{m{b}}$	$\lambda_{\max}(\exp)^b$	transitions (probability)	assignments <sup>c</sup>
345 (0.480)	312	HOMO-3 – LUMO+1 (46)	L'LCT, MLCT, IL
		HOMO-2 – LUMO (35)	IL, L'LCT, MLCT
365 (0.150)	358	HOMO – LUMO (63)	L'LCT, MLCT
		HOMO–1 – LUMO+1 (29)	L'LCT, MLCT

<sup>*a*</sup>Only transitions with a probability higher than 20% are reported. <sup>*b*</sup>In nm. <sup>*c*</sup>L = pbz, L'= Cl, L" = dppac.



Figure 5. Representative frontier orbitals and the relative composition energy levels for complex 2.

contribution of dppac. These calculations further show that LUMO and LUMO+1 are significantly localized on the pbz bridging ligand, while LUMO+2 is distributed over the dppac ligand.

# CONCLUSIONS

Reaction of [Pt(Me)(DMSO)(pbz)] with  $[Pt(Me)Cl-(DMSO)_2]$  in the presence of dppac leads to a rare tetranuclear Pt(II) complex in which two 2-(2-pyridyl)-benzimidazolate ligands act as both chelating and bridging ligands to stabilize dinuclear Pt(II) units. Dppac ligands bridging these units via P-donor atoms create a cyclic tetranuclear platinum complex. Investigation of electronic structure and related DFT and TD-DFT calculations of this tetranuclear structure indicate that the very strong near UV absorption bands have very mixed MLCT, LL'CT, and IL character.

# ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b02274.

Computational details for complex 2 (PDF)

# Accession Codes

CCDC 1874226 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge

via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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# Notes

The authors declare no competing financial interest.

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