



UNIVERSITY OF LEEDS

This is a repository copy of *Stable mixed-valent radicals from platinum(II) complexes of a bis(dioxolene) ligand.*

White Rose Research Online URL for this paper:  
<http://eprints.whiterose.ac.uk/83004/>

Version: Accepted Version

---

**Article:**

Loughrey, J, Sproules, S, McInnes, EJ et al. (2 more authors) (2014) Stable mixed-valent radicals from platinum(II) complexes of a bis(dioxolene) ligand. *Chemistry - A European Journal*, 20 (21). 6272 - 6276. ISSN 0947-6539

<https://doi.org/10.1002/chem.201304848>

---

**Reuse**

Items deposited in White Rose Research Online are protected by copyright, with all rights reserved unless indicated otherwise. They may be downloaded and/or printed for private study, or other acts as permitted by national copyright laws. The publisher or other rights holders may allow further reproduction and re-use of the full text version. This is indicated by the licence information on the White Rose Research Online record for the item.

**Takedown**

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing [eprints@whiterose.ac.uk](mailto:eprints@whiterose.ac.uk) including the URL of the record and the reason for the withdrawal request.



[eprints@whiterose.ac.uk](mailto:eprints@whiterose.ac.uk)  
<https://eprints.whiterose.ac.uk/>

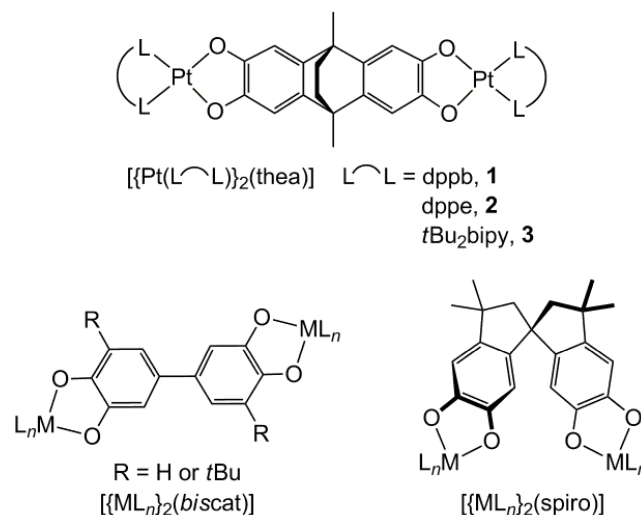
# Stable Mixed-Valent Radicals from Platinum(II) Complexes of a *Bis*-Dioxolene Ligand

Jonathan J. Loughrey,<sup>[a]</sup> Stephen Sproules,<sup>[b,c]</sup> Eric J. L. McInnes,<sup>[b]</sup> Michaele J. Hardie<sup>[a]</sup>  
and Malcolm A. Halcrow<sup>\*,[a]</sup>

**Abstract:** Three diplatinum(II) complexes  $[\{PtL\}_2(\mu\text{-thea})]$  ( $H_4\text{thea}$  = 2,3,6,7-tetrahydroxy-9,10-dimethyl-9,10-dihydro-9,10-ethanoanthracene) have been prepared, with diphosphine or bipyridyl 'L' co-ligands. One-electron oxidation of these complexes yields radical cations containing a mixed-valent  $[\text{thea}^+]\text{}^{3-}$  ligand with discrete catecholate and semiquinone centers separated by quaternary methylene spacers. The electronic character of these radicals is near the Robin/Day class II/III border by UV/vis/NIR and EPR spectroscopy. Crystal structure determinations and a DF calculation imply that oxidation of the  $\text{thea}^{4-}$  ligand may lead to an increased through-space interaction between the dioxolene  $\pi$ -systems.

Metal complexes of dioxolenes can exhibit a fascinating ligand-based redox chemistry, involving conversion between catecholate ('cat'), semiquinone ('sq') and quinone ('q') ligand oxidation levels.<sup>[1-3]</sup> Complexes of dinucleating dioxolenes add another layer of complexity to this behaviour with multiple metal and ligand redox sites,<sup>[2-4]</sup> which may give rise to ligand-based mixed-valency.<sup>[5]</sup> One example is 4,4'-*biscatechol* ( $H_4\text{biscat}$ , Scheme 1) whose derivatives form delocalized radicals at the sq/cat oxidation state, but are spin-coupled at the sq/sq level reflecting formal oxidation of the central C-C bond.<sup>[6-8]</sup> Conversely, cat/sq radicals generated from spiro<sup>4-</sup> complexes ( $H_4\text{spiro}$  = 3,3,3',3'-tetramethyl-1,1'-spirobis-{5,6-dihydroxyindane}, Scheme 1) are localized on individual dioxolene rings,<sup>[2]</sup> with electron hopping between the dioxolene groups occurring near the EPR timescale.<sup>[9]</sup> Transition metal dioxolene complexes can also exhibit valence tautomerism and spin transition equilibria involving metal $\rightleftharpoons$ ligand charge transfer,<sup>[10]</sup> but few examples of these phenomena in *bis*-dioxolene ligand systems have been reported to date.<sup>[2,9,11]</sup>

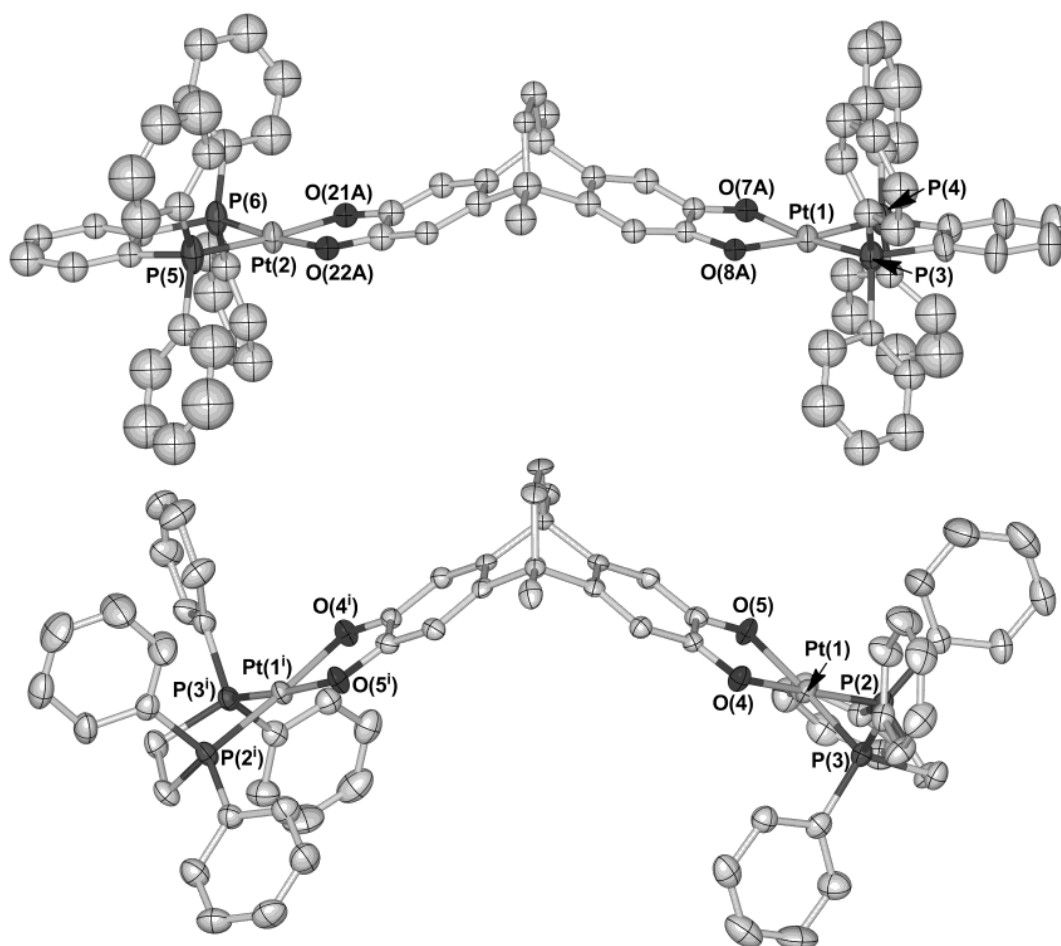
We report here the redox chemistry of 2,3,6,7-tetrahydroxy-9,10-dimethyl-9,10-dihydro-9,10-ethanoanthracene ( $H_4\text{thea}$ ) when complexed to platinum(II) (**1-3**, Scheme 1). Others have used  $\text{thea}^{4-}$  as a component in metallacycle and cage complexes, but the redox chemistry of those products was not reported.<sup>[12,13]</sup> The dimethyl-bicyclo[2.2.2]octyl spacer prevents formal conjugation of the  $\text{thea}^{n-}$  dioxolene groups but places them close in space. We therefore predicted that the cat/sq species  $[\text{thea}^+]\text{}^{3-}$  should exhibit mixed-valence behavior intermediate between  $[\text{biscat}^+]\text{}^{3-}$  and  $[\text{spiro}^+]\text{}^{3-}$  (Scheme 1).



**Scheme 1.** The compounds reported in this work, and other complexes referred to in the discussion. Co-ligand abbreviations: dppb = 1,2-*bis*(diphenylphosphino)benzene; dppe = 1,2-*bis*(diphenyl-phosphino)ethane; *t*Bu<sub>2</sub>bipy = 4,4'-*bis*(*tert*butyl)-2,2'-bipyridyl.

- [a] Dr. J. J. Loughrey, Prof M. J. Hardie, Prof M. A. Halcrow  
School of Chemistry, University of Leeds, Woodhouse Lane, Leeds,  
LS2 9JT (UK)  
Fax: (+44) 113 343 6565  
E-mail: m.a.halcrow@leeds.ac.uk  
Homepage: <http://www.chem.leeds.ac.uk/People/Halcrow.html>
- [b] Dr. S. Sproules, Prof E. J. L. McInnes  
School of Chemistry and Photon Science Institute, University of  
Manchester, Oxford Road, Manchester, M13 9PL (UK)
- [c] Current address: School of Chemistry, University of Glasgow, Joseph  
Black Building, University Avenue, Glasgow, G12 8QQ (UK)
- Supporting information for this article is available on the WWW under  
<http://dx.doi.org/10.1002/chem.201xxxxx>.

The synthesis of **1-3** was achieved by reacting  $H_4\text{thea}$  with 2 equiv of preformed  $[PtCl_2L]$  ( $L$  = dppb, dppe or *t*Bu<sub>2</sub>bipy) in the presence of base. The complexes can be handled in air in the solid state and in solution, but must be stored under an inert atmosphere for extended periods. X-ray structure determinations of **1** and **2** were achieved from solvate crystals grown from dichloromethane/pentane (Fig. 1). Although both structures are crystallographically non-routine,<sup>[14]</sup> the metric parameters about the  $\text{thea}^{4-}$  ligands confirm that the dioxolene rings are at the catecholate oxidation level ( $-1.7(3) \geq \Delta \geq -2.1(2)$ ),<sup>[15]</sup> Table 1). The dihedral angle between the  $\text{thea}^{4-}$  dioxolene groups ( $\theta$ , Table 1) is *ca.*  $10^\circ$  larger in **2** than in **1**, showing there is some conformational flexibility in the  $\text{thea}^{4-}$  framework.



**Figure 1.** The 'A' disorder site of the  $[\{\text{Pt}(\text{dppb})\}_2(\text{thea})]$  molecule in  $1 \cdot x\text{C}_5\text{H}_{12} \cdot (4-x)\text{CH}_2\text{Cl}_2$  (top),<sup>[12]</sup> and the  $[\{\text{Pt}(\text{dppe})\}_2(\text{thea})]^+$  cation in  $[\mathbf{2}]\text{PF}_6 \cdot 3\text{CH}_2\text{Cl}_2$  (bottom). Displacement ellipsoids are at the 50 % probability level, and all H atoms have been omitted for clarity. Symmetry code: (i)  $3/2-x, 1/2-y, z$ . Additional crystallographic Figures and Tables are in the Supporting Information.<sup>[16]</sup>

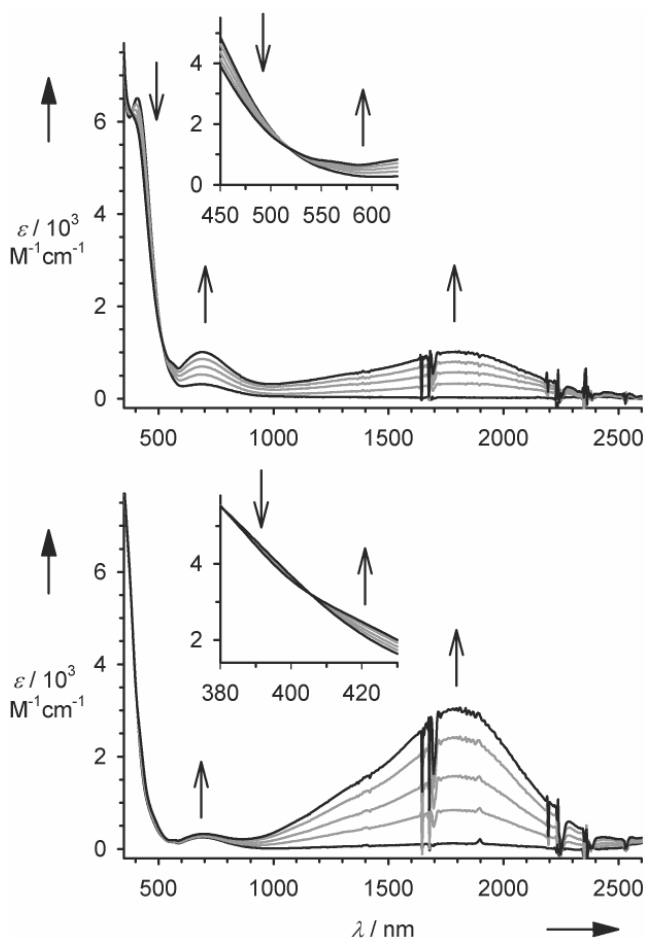
**Table 1.** Selected metric parameters from the crystal structures in this work.  $\Delta$  is a bond-valence sum parameter giving the oxidation state of dioxolene groups, which takes the values of 0, -1 and -2 for the q, sq and cat levels respectively.<sup>[15]</sup>  $\theta$  is the dihedral angle between the least squares planes of the  $\text{thea}^{4+}$  dioxolene rings. More detailed information about the structures is given in the Supporting Information.

	Pt-O [Å]	Pt-P [Å]	$\Delta$	$\theta$ [°]
1	1.98(2)–2.05(2)	2.201(3)–2.207(3)	$-1.7(3) \geq \Delta \geq -1.9(2)^{[a]}$	140.8(5)–141.1(5) <sup>[a]</sup>
2 molecule A	2.026(8)–2.048(8)	2.202(4)–2.227(3)	-1.77(15), -2.1(2)	130.8(5)
molecule B	2.006(13)–2.049(9)	2.205(4)–2.236(4)	-1.86(14), -2.1(2)	131.1(6)
molecule C	2.034(9)–2.071(15)	2.195(6)–2.222(4)	-1.90(15) <sup>[b]</sup>	129.8(9)–131.5(6) <sup>[a]</sup>
$[\mathbf{2}]\text{PF}_6^{[c]}$	2.042(4), 2.060(4)	2.2101(14), 2.2197(14)	-1.57(15)	117.14(11)

[a] Range of values given for disorder sites in this residue.<sup>[14]</sup> [b]  $\Delta$  for the second Pt/dioxolene center in this molecule was not determined, because of restraints applied in the crystallographic refinement. [c] There is only one unique Pt/dioxolene center in this crystal structure.<sup>[14]</sup>

Cyclic and differential pulse voltammetry of **1-3** in  $\text{CH}_2\text{Cl}_2/0.5 \text{ M } n\text{Bu}_4\text{NPF}_6$  at 298 K revealed two chemically reversible low-potential oxidations at  $-0.37 \pm 0.02$  and  $-0.11 \pm 0.02$  V vs.  $[\text{FeCp}_2]/[\text{FeCp}_2]^+$ .<sup>[16]</sup> These were assigned to the  $[\text{thea}]^{4+} \rightleftharpoons [\text{thea}]^{3+} \rightleftharpoons [\text{thea}^{**}]^{2+}$  (cat/cat  $\rightleftharpoons$  cat/sq  $\rightleftharpoons$  sq/sq) redox series. The

separation of these processes ( $\Delta E$ ) is  $250 \pm 20$  mV, between complexes of  $\text{biscat}^{4+}$  ( $\Delta E = 320\text{--}500$  mV)<sup>[2,6,7]</sup> and of  $\text{spiro}^{4+}$  (140–170 mV).<sup>[2,9]</sup> The subsequent  $[\text{thea}^{**}]^{2+} \rightleftharpoons [\text{thea}^*]^- \rightleftharpoons [\text{thea}]^0$  (sq/sq  $\rightleftharpoons$  sq/q  $\rightleftharpoons$  q/q) oxidations occurred near +0.75 V, were more closely separated ( $\Delta E \leq 110$  mV) and were only partly reversible at room temperature.



**Figure 2.** UV/vis/NIR titrations for the chemical oxidation of **1** (top) and **2** (bottom) by up to 1 equiv [FeCp<sub>2</sub>]PF<sub>6</sub> (CH<sub>2</sub>Cl<sub>2</sub>, 296 K). The spectra of pure **1**, [1]<sup>+</sup>, **2** and [2]<sup>+</sup> are highlighted as black lines while the intermediate stoichiometries are paler. Isosbestic points are shown as insets.<sup>[16]</sup>

The green oxidized products [1]<sup>+</sup> and [2]<sup>+</sup>, and purple [3]<sup>+</sup>, can be generated by treatment of the neutral precursors with 1 equiv [FeCp<sub>2</sub>]PF<sub>6</sub> in CH<sub>2</sub>Cl<sub>2</sub>. Solutions of [1]<sup>+</sup> and [2]<sup>+</sup> are stable for hours at 298 K under an inert atmosphere, which allowed [1]PF<sub>6</sub> and [2]PF<sub>6</sub> to be isolated and crystallized (see below), but [3]PF<sub>6</sub> decomposes slowly under those conditions. The oxidations were monitored by UV/vis/NIR titrations, which proceeded isosbesticly for **1** and **2** (Fig. 2). In both cases, ingrowth of a new IVCT transition at 1810 nm with at least one low-wavelength shoulder was observed, along with a smaller increase in intensity of the dioxolene→L (L = dppb or dppe) LLCT band near 690 nm.<sup>[13]</sup> The intensity of the IVCT band is around 3 times greater in [2]<sup>+</sup> than in [1]<sup>+</sup>. An IVCT band with λ<sub>max</sub> = 1917 nm is also formed during the oxidation of **3**, reaching ε<sub>max</sub> = 6.3 × 10<sup>3</sup> M<sup>-1</sup>cm<sup>-1</sup> for [3]<sup>+</sup> which is twice as intense as that exhibited by [2]<sup>+</sup> (Fig. 2). That titration was not isosbestic, however, which indicates slow decomposition of [3]<sup>+</sup> under these conditions.

The width at half height, Δν<sub>1/2</sub>, of the IVCT bands in [1]<sup>+</sup> and [2]<sup>+</sup> is ≤ 2300 cm<sup>-1</sup>, taking account of the low-wavelength shoulder. That is smaller than predicted by eq 1 for [1]<sup>+</sup> and [2]<sup>+</sup>, which affords Δν<sub>1/2</sub> ≈ 3550 cm<sup>-1</sup> for a class II mixed-valent system with an IVCT maximum of 1810 nm (E = 5525 cm<sup>-1</sup>).<sup>[17]</sup>

$$\Delta\nu_{1/2} = (2310E)^{1/2} \quad (1)$$

Although this criterion should be applied with care, the [thea]<sup>3-</sup> framework is clearly approaching the class III formalism. In the class III limit, the electron coupling energy H<sub>AB</sub> for [1]<sup>+</sup> and [2]<sup>+</sup> is approximately 1150 cm<sup>-1</sup> according to eq 2.<sup>[5,17]</sup>

$$H_{AB} = \frac{1}{2}\Delta\nu_{1/2} \quad (2)$$

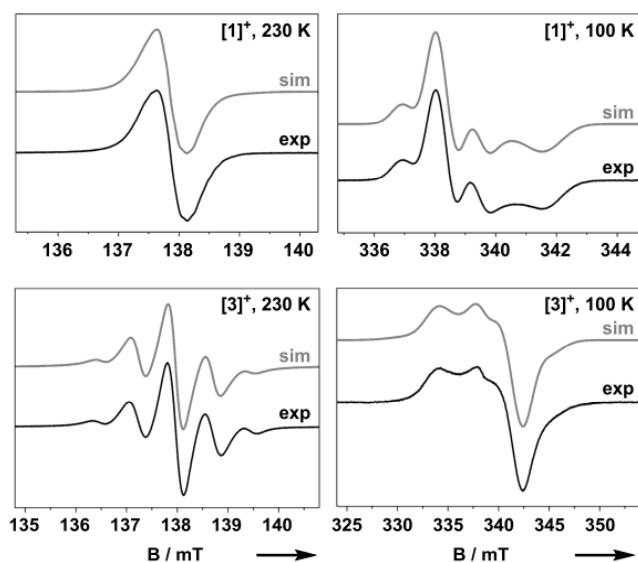
That is comparable to cyclophane radical ions and related species, which show through-space coupling between stacked aromatic rings.<sup>[18]</sup> Solutions of [2]<sup>+</sup> exhibit a correlation between the IVCT maximum and the donor number of the solvent,<sup>[19]</sup> in the order dmf (λ<sub>max</sub> = 1883 nm) > thf (1847) > acetone (1829) > CH<sub>2</sub>Cl<sub>2</sub> (1810). The maximum variation in IVCT energy between these solvents (215 cm<sup>-1</sup>) is smaller than expected for a class II organic radical,<sup>[20]</sup> and again implies a degree of delocalization between the [thea]<sup>3-</sup> dioxolene groups.<sup>[5]</sup> The IVCT linewidth Δν<sub>1/2</sub> does not vary significantly in these spectra, but the relative intensities of the IVCT band and the MLCT absorption near 700 nm show a much stronger solvent dependence.<sup>[16]</sup>

The S-band and X-band EPR spectra of [1]<sup>+</sup> and [2]<sup>+</sup> in 10:1 CH<sub>2</sub>Cl<sub>2</sub>:THF fluid solution are very similar, with g-values close to that of the free-electron (Table 2, Fig. 3). Although hyperfine coupling was not clearly resolved, features on the S-band lineshape could be modelled by considering hyperfine coupling to two <sup>195</sup>Pt (I = 1/2, % abundant) and four <sup>31</sup>P (I = 1/2, 100% abundant) nuclei. The spectrum of [3]<sup>+</sup> contains five resolved lines, that more obviously arise from hyperfine coupling to two <sup>195</sup>Pt nuclei. This demonstrates electron hopping between the [thea]<sup>3-</sup> dioxolene rings, that is rapid on the EPR timescale at these temperatures. The X-band linewidths of [1]<sup>+</sup> and [2]<sup>+</sup> are almost invariant between 200–300 K, but the spectrum of [3]<sup>+</sup> broadens considerably below 230 K, which could indicate the slowing of this electron hopping<sup>[9]</sup> and/or aggregation of the complex in solution (see below).<sup>[16]</sup> In contrast, frozen solution X-band spectra of [1]<sup>+</sup>-[3]<sup>+</sup> are near-axial and show coupling to just one <sup>195</sup>Pt nucleus, and for [1]<sup>+</sup> and [2]<sup>+</sup>, two <sup>31</sup>P nuclei (Fig. 3). Therefore electron hopping between their dioxolene groups is frozen out, apparently coinciding with freezing of the solvent medium.<sup>[9]</sup> Although the hyperfine coupling for [3]<sup>+</sup> is poorly resolved in the frozen solution spectrum, the g-anisotropy and <sup>195</sup>Pt couplings in [3]<sup>+</sup> are over double those in [1]<sup>+</sup> and [2]<sup>+</sup>. This indicates a greater Pt contribution to the frontier orbital in the presence of the more strongly π-accepting tBu<sub>2</sub>bipy ligand.<sup>[21]</sup>

**Table 2.** Simulated EPR spectroscopic parameters for [1]<sup>+</sup>-[3]<sup>+</sup> in 10:1 CH<sub>2</sub>Cl<sub>2</sub>:thf solution. Hyperfine couplings are to <sup>195</sup>Pt, and are in 10<sup>-4</sup> cm<sup>-1</sup>.

	210 K g (A <sup>[a]</sup> )	100 K g <sub>1</sub> (A <sub>1</sub> <sup>[b]</sup> )	g <sub>2</sub> (A <sub>2</sub> <sup>[b]</sup> )	g <sub>3</sub> (A <sub>3</sub> <sup>[b]</sup> )
[1] <sup>+</sup> [c]	2.0011 (4.9)	2.0045 (20)	2.0031 (19)	1.9844 (-10)
[2] <sup>+</sup> [c]	2.0012 (4.7)	2.0055 (19.5)	2.0032 (19)	1.9833 (-10)
[3] <sup>+</sup>	2.0019 (13.5)	2.0292 (48)	1.9872 (48)	1.9796 (40)

[a] Coupling to two <sup>195</sup>Pt nuclei. [b] Coupling to one <sup>195</sup>Pt nucleus. [c] An additional superhyperfine coupling of 1-3 × 10<sup>-4</sup> cm<sup>-1</sup> to <sup>31</sup>P nuclei can also be extracted from the lineshapes of these spectra.



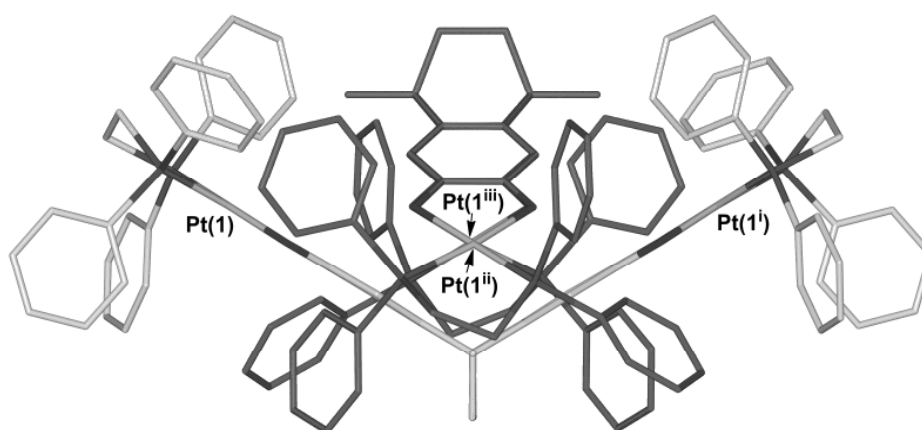
**Figure 3.** Fluid solution S-band, and frozen solution X-band, EPR spectra of  $[1]^+$  and  $[3]^+$  in 10:1  $\text{CH}_2\text{Cl}_2$ :thf. Simulation parameters are given in Table 2.<sup>[16]</sup>

Single crystal X-ray structures were obtained of  $[2]\text{PF}_6 \cdot 3\text{CH}_2\text{Cl}_2$  and a solvate of  $[1]\text{PF}_6$ , although the latter structure is of too low resolution for a detailed analysis of its metric parameters.<sup>[14]</sup> The complex cation in  $[2]\text{PF}_6 \cdot 3\text{CH}_2\text{Cl}_2$  has crystallographic  $C_2$  symmetry, meaning that the oxidized and unoxidized dioxolene groups are crystallographically equivalent (Fig. 1). While the bond lengths to the Pt atom are indistinguishable from the neutral complexes, the metric parameters in the unique dioxolene center are consistent with a singly oxidized  $[\text{thea}^{\cdot+}]^3$  ligand ( $\Delta = -1.57(15)$ , Table 1; the expected value is  $-1.5$ <sup>[15]</sup>). The dihedral angle between the dioxolene groups ( $\theta$ ) in  $[2]^+$  is contracted to  $117.14(11)^\circ$ , *ca.*  $14^\circ$  lower than in **2** (Table 1; the corresponding values for the two

unique complex cations in  $[1]\text{PF}_6$  are  $108.7(5)$  and  $112.8(7)^\circ$ . While they are not isomorphous, in both structures the radical cations associate into nested dimers (Fig. 4). The assignment of these dimers as charge-transfer assemblies is uncertain, since there are no interatomic contacts between the nested molecules shorter than the sum of their van der Waals radii. However, a dimerization equilibrium of this type could explain the EPR line-broadening observed for  $[3]^+$  below 230 K.<sup>[16]</sup> Notably, unoxidized **1** and **2** do not dimerize in this manner in the crystals of those compounds. The  $\text{PF}_6^-$  ions in both radical structures only associate with the cations through peripheral van der Waals contacts.<sup>[14,16]</sup>

A DF calculation of the model complex  $[\{\text{Pt}(\text{bipy})\}_2(\text{thea})]$  showed that the HOMO lies predominantly on the  $\text{thea}^{4+}$  ligand and has  $\pi$ -antibonding character between the two dioxolene rings.<sup>[16]</sup> The reduced  $\theta$  values in  $[1]\text{PF}_6$  and  $[2]\text{PF}_6$  compared to **1** and **2** (Table 1) are consistent with depopulation of this HOMO upon oxidation, which would strengthen any bonding interaction between the dioxolene groups. The HOMO-1 is the corresponding in-phase combination between the  $\text{thea}^{4+}$  dioxolene rings. The calculated energy gap between the HOMO and HOMO-1, 0.24 V, is a good match for the electrochemical separation between the cat/sq oxidations in **1-3** ( $\Delta E \approx 250$  mV).

In conclusion, oxidation of **1-3** affords  $[\text{thea}^{\cdot+}]^3$  radical derivatives. Although their dioxolene centers are not directly conjugated,  $[1]^+ - [3]^+$  show electron-hopping between the dioxolene rings in fluid solution by EPR, and a degree of electron delocalization that is comparable to cyclophane-derived radicals.<sup>[18]</sup> The strength of this electron coupling may reflect the proximity of the dioxolene rings, which are only  $2.4 \text{ \AA}$  apart at their closest approach in  $[2]\text{PF}_6$ . More detailed spectroscopic and theoretical studies are in progress to characterize the other redox states of **1-3**, and to clarify the electronic structures of radical species based on  $\text{thea}^{n+}$  and related *bis*- and *tris*-dioxolenes.



**Figure 4.** View of the association of the radical cations in  $[2]\text{PF}_6 \cdot 3\text{CH}_2\text{Cl}_2$  into nested dimers, generated from the unique half-molecule by crystallographic  $S_4$  symmetry. The C atoms of the two molecules have pale and dark coloration, and H atoms have been omitted for clarity. Pt( $1^{ii}$ ) is at the front of the figure, while Pt( $1^{iii}$ ) is directly behind it. Symmetry codes: (i)  $3/2-x, 1/2-y, z$ ; (ii)  $1/2+y, 1-x, 1-z$ ; (iii)  $1-y, -1/2+x, 1-z$ .

## Experimental Section

Synthetic procedures and characterization data for **1-3**, and details of the instrumentation and computational procedures used for the spectroscopic and electrochemical measurements, crystal structure determinations and DF calculation, are given in the Supporting Information.<sup>[16]</sup>

## Acknowledgements

This work was supported by the EPSRC. We thank Diamond Light Source for access to beamline I19 (MT8517) that contributed to the results presented here.

**Keywords:** mixed-valent compounds • charge transfer • radical ions • platinum • dioxolene

- [1] C. G. Pierpont, C. W. Lange, *Prog. Inorg. Chem.* **1993**, *41*, 331–442.
- [2] A. Dei, D. Gatteschi, C. Sangregorio, L. Sorace, *Acc. Chem. Res.* **2004**, *37*, 827–835
- [3] J. S. Miller, K. S. Min, *Angew. Chem.* **2009**, *121*, 268–278; *Angew. Chem. Int. Ed.* **2009**, *48*, 262–272.
- [4] Other bis-dioxolene radical complexes have also been investigated as molecular magnets. a) A. Caneschi, A. Dei, H. Lee, D. A. Shultz, L. Sorace, *Inorg. Chem.* **2001**, *40*, 408–411; b) D. A. Shultz, S. H. Bodnar, H. Lee, J. W. Kampf, C. D. Incarvito, A. L. Rheingold, *J. Am. Chem. Soc.* **2002**, *124*, 10054–10061; c) D. A. Shultz, R. M. Fico jr., S. H. Bodnar, R. K. Kumar, K. E. Vostrikova, J. W. Kampf, P. D. Boyle, *J. Am. Chem. Soc.* **2003**, *125*, 11761–11771; d) J. C. Sloop, D. A. Shultz, T. Coote, B. Shepler, U. Sullivan, J. W. Kampf, P. D. Boyle, *J. Phys. Org. Chem.* **2012**, *25*, 314–321.
- [5] a) J. Hankache, O. S. Wenger, *Chem. Rev.* **2011**, *111*, 5138–5178; b) A. Heckmann, C. Lambert, *Angew. Chem.* **2012**, *124*, 334–404; *Angew. Chem. Int. Ed.* **2012**, *51*, 326–392.
- [6] a) L. F. Joulí, E. Schatz, M. D. Ward, F. Weber, L. J. Yellowlees, *J. Chem. Soc. Dalton Trans.* **1994**, 799–804; b) A. M. Barthram, Z. R. Reeves, J. C. Jeffery, M. D. Ward, *J. Chem. Soc. Dalton Trans.* **2000**, 3162–3169.
- [7] J. Best, I. V. Sazanovich, H. Adams, R. D. Bennett, E. S. Davies, A. J. H. M. Meijer, M. Towrie, S. A. Tikhomirov, O. V. Bouganov, M. D. Ward, J. A. Weinstein, *Inorg. Chem.* **2010**, *49*, 10041–10056.
- [8] A. Bencini, C. A. Daul, A. Dei, F. Mariotti, H. Lee, D. A. Shultz, L. Sorace, *Inorg. Chem.* **2001**, *40*, 1582–1590.
- [9] K. G. Alley, G. Poneti, P. S. D. Robinson, A. Nafady, B. Moubaraki, J. B. Aitken, S. C. Drew, C. Ritchie, B. F. Abrahams, R. K. Hocking, K. S. Murray, A. M. Bond, H. H. Harris, L. Sorace, C. Boskovic, *J. Am. Chem. Soc.* **2013**, *135*, 8304–8323.
- [10] a) C. G. Pierpont, *Coord. Chem. Rev.* **2001**, *216–217*, 99–125; b) D. N. Hendrickson, C. G. Pierpont, *Top. Curr. Chem.* **2004**, *234*, 63–95; c) C. G. Pierpont, *Inorg. Chem.* **2011**, *50*, 9766–9772.
- [11] a) A. Beni, A. Dei, D. A. Shultz, L. Sorace, *Chem. Phys. Lett.* **2006**, *428*, 400–404; b) M. Affronte, A. Beni, A. Dei, L. Sorace, *Dalton Trans.* **2007**, 5253–5259; c) K. G. Alley, G. Poneti, J. B. Aitken, R. K. Hocking, B. Moubaraki, K. S. Murray, B. F. Abrahams, H. H. Harris, L. Sorace, C. Boskovic, *Inorg. Chem.* **2012**, *51*, 3944–3946.
- [12] P. Thuéry, B. Masci, *Supramol. Chem.* **2003**, *15*, 95–99.
- [13] B. F. Abrahams, N. J. FitzGerald, R. Robson, *Inorg. Chem.* **2010**, *49*, 5953–5956.
- [14] The complex molecule in  $1-x\text{C}_3\text{H}_{12}\cdot(4-x)\text{CH}_2\text{Cl}_2$  is disordered across a non-crystallographic mirror plane. The crystal also contains channels of disordered solvent. The asymmetric unit of  $2\cdot 0.67\text{H}_2\text{O}\cdot 2.07\text{CH}_2\text{Cl}_2$  contains three unique complex molecules, which also contain some disorder. Solvated  $[\mathbf{1}]\text{PF}_6^-$  contains two unique complex half-molecules with crystallographic  $C_2$  symmetry. The  $\text{PF}_6^-$  ions occupy defined lattice sites, but the unit cell contains 26 % disordered void space making the crystals poor diffractors of X-rays. The complex cation in  $[\mathbf{2}]\text{PF}_6\cdot 3\text{CH}_2\text{Cl}_2$  also has crystallographic  $C_2$  symmetry. The anions and solvent lie in disordered sheets between layers of the cations, although the anion sites were clearly resolved in the Fourier map.<sup>[16]</sup>
- [15] O. Carugo, C. B. Castellani, K. Djinović, M. Rizzi, *J. Chem. Soc. Dalton Trans.* **1992**, 837–841.
- [16] Additional Tables and Figures of the voltammetry, EPR and UV-vis/NIR data, the crystal structures and the DF calculation are given in the Supporting Information.
- [17] K. D. Demadis, C. M. Hartshorn, T. J. Meyer, *Chem. Rev.* **2001**, *101*, 2655–2685.
- [18] See e.g. a) D. Sun, S. V. Rosokha, J. K. Kochi, *J. Am. Chem. Soc.* **2004**, *126*, 1388–1401; b) P. H. Dinolfo, V. Coropceanu, J. L. Brédas, J. T. Hupp, *J. Am. Chem. Soc.* **2006**, *128*, 12592–12593.
- [19] Y. Marcus, *Chem. Soc. Rev.* **1993**, *22*, 409–416.
- [20] See e.g. S. F. Nelsen, D. A. Trieber II, R. F. Ismagilov, Y. Teki, *J. Am. Chem. Soc.* **2001**, *123*, 5684–5694.
- [21] a) E. J. L. McInnes, R. D. Farley, S. A. Macgregor, K. J. Taylor, L. J. Yellowlees, C. C. Rowlands, *J. Chem. Soc. Faraday Trans.* **1998**, *94*, 2985–2991; b) E. J. L. McInnes, R. D. Farley, C. C. Rowlands, A. J. Welch, L. Rovatti, L. J. Yellowlees, *J. Chem. Soc. Dalton Trans.* **1999**, 4203–4208.