


 Cite this: *Chem. Commun.*, 2018, 54, 11284

 Received 11th July 2018,  
 Accepted 18th September 2018

DOI: 10.1039/c8cc05591b

rsc.li/chemcomm

# The semiquinone radical anion of 1,10-phenanthroline-5,6-dione: synthesis and rare earth coordination chemistry†

 James R. Hickson,<sup>ab</sup> Samuel J. Horsewill,<sup>a</sup> Jake McGuire,<sup>id a</sup> Claire Wilson,<sup>id a</sup> Stephen Sproules<sup>id \*a</sup> and Joy H. Farnaby<sup>id \*a</sup>

**Reduction of 1,10-phenanthroline-5,6-dione (pd) with CoCp<sup>R</sup><sub>2</sub> resulted in the first molecular compounds of the pd<sup>•−</sup> semi-quinone radical anion, [CoCp<sup>R</sup><sub>2</sub>]<sup>+</sup>[pd]<sup>•−</sup> (R = H, (1); R = Me<sub>4</sub>, (2)). Furthermore compounds 1 and 2 were reacted with [Y(hfac)<sub>3</sub>(thf)<sub>2</sub>] (hfac = 1,1,1-5,5,5-hexafluoroacetylacetonate) to synthesise the rare earth-transition metal heterometallic compounds, [CoCp<sup>R</sup><sub>2</sub>]<sup>+</sup>[Y(hfac)<sub>3</sub>-(N,N'-pd)]<sup>•−</sup> (R = H, (3); R = Me<sub>4</sub>, (4)).**

Electron transfer reactions are fundamental to chemical processes. Stable organic and organometallic radicals are widely utilised, particularly in small molecule activation and catalysis.<sup>1</sup> Redox-active ligands can act as electron reservoirs to achieve two electron processes, such as oxidative addition or reductive elimination, that would otherwise be inaccessible. This is a successful strategy in transition metal chemistry for the replacement of precious metals with earth abundant metals<sup>2</sup> and has also been demonstrated for the f-elements.<sup>3,4</sup>

The most common use of a f-element radical is the use of samarium diiodide in organic chemistry. However, organometallic complexes of the f-elements have proved particularly suited for the reductive activation and stabilisation in well-defined molecular complexes, of some of the most unusual and biologically relevant radical species *e.g.* CO<sup>•−</sup>, CO<sub>2</sub><sup>•−</sup> and NO<sup>•−</sup>.<sup>5–7</sup> The number of examples of f-elements complexed to redox-active ligands or radical anions is still modest but this is a growing area of research activity; for magnetism, multi-electron transfer chemistry and functional materials.<sup>4,8</sup> Heterobimetallic complexes remain a particular synthetic challenge. In order to realise mixed-metal complexes, a bridging ligand with different coordination sites is needed so that metal ions can be selected and installed step-wise to acquire the desired properties. However, the

bridging ligands used in f-element chemistry have identical binding sites that lead near exclusively to homobimetallic complexes.

Phenanthroline dione (pd) is a commercially available yet highly underutilised redox-active ligand. It constitutes a three-membered electron transfer series, where the neutral form can be sequentially, one-electron reduced to give the monoanionic and dianionic forms (Scheme 1). The terminal members are diamagnetic, whereas the monoanionic form is a radical with an *S* = 1/2 ground state. The most prized features of this ligand are its two binding sites. In the dianionic form of the ligand (right, Scheme 1), the *N,N'*-pocket is a  $\pi$ -accepting diimine unit analogous to 2,2'-bipyridine, and distinct from the *O,O'*-pocket which is a  $\pi$ -donating diolate, akin to a catecholate.

There is literature precedent for the formation of multi-metallic complexes using the dianionic form of the ligand.<sup>9–12</sup> We also recently reported heterometallic rare earth-transition metal complexes utilising pd as a template.<sup>13</sup> Our two-step route was necessary because although pd is reported to react with a number of reducing agents, the products are insoluble in common solvents, precluding collection of spectroscopic data and definitive assignment of redox state, but more importantly further reactivity.<sup>11,14,15</sup>

In contrast to the well-developed chemistry of transition metal semiquinones,<sup>16</sup> there are only three reports of the *in situ* characterisation of pd<sup>•−</sup>.<sup>17–19</sup> These include two spectro-electrochemical studies in combination with EPR, and an EPR study.

Here we report the first organometallic synthons of the radical anion of pd, [CoCp<sup>R</sup><sub>2</sub>]<sup>+</sup>[pd]<sup>•−</sup> (R = H, (1); R = Me<sub>4</sub>, (2)).



**Scheme 1** Three-membered electron transfer series for pd showing calculated bond distances.

<sup>a</sup> School of Chemistry, WestCHEM, University of Glasgow, Glasgow, UK.  
 E-mail: joy.farnaby@glasgow.ac.uk, Stephen.sproules@glasgow.ac.uk

<sup>b</sup> Department of Chemistry, Imperial College London, South Kensington, London, UK

† Electronic supplementary information (ESI) available. CCDC 1854232 and 1854233. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8cc05591b





Scheme 2 Synthetic route to radical anion containing rare-earth transition metal complexes.

Furthermore, we demonstrate the coordination chemistry of **1** and **2**, with  $[\text{Y}(\text{hfac})_3(\text{thf})_2]$  ( $\text{hfac} = 1,1,1\text{-}5,5,5\text{-hexafluoroacetylacetonate}$ ) to synthesise the rare earth-transition metal heterometallic compounds,  $[\text{CoCpR}_2]^+[\text{Y}(\text{hfac})_3(\text{N,N}'\text{-pd})]^-$  ( $\text{R} = \text{H}$ , (**3**);  $\text{R} = \text{Me}$ , (**4**)). Our first choice of synthon for this chemistry was the potassium salt of  $\text{pd}^{\bullet-}$ , formed by reduction of  $\text{pd}$  with  $\text{KH}$  (see ESI†). However, while the spectroscopic data are consistent with  $[\text{K}^+][\text{pd}^{\bullet-}]$ , its synthetic utility is limited. The reductants  $\text{CoCpR}_2$  were therefore selected to promote the formation of solvent separated ion pairs.

Complexes **1** and **2** were synthesised by the cold addition of a solution of  $\text{CoCpR}_2$  to a suspension of  $\text{pd}$ , both in acetonitrile. Complexes **1** and **2** were isolated after work-up as dark purple solids in good yields of 93% and 61%, respectively (Scheme 2). The lower yield of **2** is attributed to the  $\text{CoCp}^t_2$  being generated *in situ*. The subsequent addition of a solution of  $[\text{Y}(\text{hfac})_3(\text{thf})_2]$  to a solution of either **1** (RT) or **2** ( $-35^\circ\text{C}$ ) resulted in an immediate colour change from dark purple to dark green. After work-up, the heterometallic complexes **3** and **4** were isolated as dark green solids in good yields of 65% and 83%, respectively (Scheme 2). The purity of **1–4** were confirmed by elemental analysis and all complexes were fully characterised (see ESI† for full experimental details and spectra).

The  $^1\text{H}$  NMR spectra of **1** and **2** in  $d_3\text{-MeCN}$  at room temperature are consistent with  $[\text{CoCpR}_2]^+$  and display no other resonances. In addition to the  $[\text{CoCpR}_2]^+$  resonances, the  $^1\text{H}$  NMR spectra of **3** in  $d_3\text{-MeCN}$  and **4** in  $d_8\text{-THF}$  at room temperature display both broadened proton environments in the  $\text{pd}^{\bullet-}$  region and  $\text{hfac}$  singlets (this latter in the appropriate ratio for the 1 : 1 adduct). These data are consistent with remote *i.e.*  $\text{N,N}'$ -binding to  $\text{pd}^{\bullet-}$ . The ATR IR spectra of **1** and **2** are also consistent with the reduction of  $\text{pd}$  to  $\text{pd}^{\bullet-}$ . The  $\nu_{\text{CO}}$  of neutral  $\text{pd}$  of  $1678\text{ cm}^{-1}$  is no longer visible and there are two strong absorptions in the expected range for semiquinone radicals ( $1500\text{--}1400\text{ cm}^{-1}$ ) at  $1511\text{ cm}^{-1}$  and  $1485\text{ cm}^{-1}$ .<sup>11,15</sup> The ATR IR spectrum of  $[\text{K}(\text{DME})_x]^+[\text{pd}^{\bullet-}]$  ( $\text{DME} = \text{dimethoxyethane}$ , see ESI†), which does not contain aromatic  $\nu_{\text{CC}}$  also displays two strong absorptions at  $1518\text{ cm}^{-1}$  and  $1504\text{ cm}^{-1}$ . We therefore assign both absorptions in **1** and **2**, centred *ca.*  $1500\text{ cm}^{-1}$  to the symmetric and asymmetric stretch of the semiquinone. The ATR IR of **3** and **4** also contain multiple strong absorptions in the semiquinone region, however, their assignment cannot be definitive since the ancillary ligand vibrations from  $\text{hfac}$  also occur in the same region. There are no absorptions in catecholate region, consistent with  $\text{N,N}'$ -binding. Electronic spectra of **1–4** were collected in MeCN or THF (see ESI†) and

are consistent with electrochemically generated  $\text{pd}^{\bullet-}$ .<sup>17–19</sup> Time dependent (TD) density functional (DFT) calculations have been used to assign the electronic spectra (*vide infra*).

Single crystals of **1** suitable for X-ray diffraction were grown from acetonitrile solution at  $-35^\circ\text{C}$ , over two weeks. The solid state molecular structure and selected parameters are shown in Fig. 1. These data represent the first structural data available for  $\text{pd}^{\bullet-}$ . The metrics important for assessing the redox state of the ligand are those of the  $\text{O,O}'$ -pocket. In particular the bond distances of  $\text{C5-O1}$   $1.268(4)\text{ \AA}$  and  $\text{C6-O2}$   $1.278(4)\text{ \AA}$  in **1** are identical within error to one another and intermediate in length between a C–O double bond ( $\text{pd}^0$ ,  $\text{C6-O2}$   $1.23(2)$  and  $\text{C5-O1}$   $1.24(2)\text{ \AA}$ ) and a C–O single bond ( $\text{pd}^{2-}$ ,  $\text{C6-O2}$   $1.35(1)$  and  $\text{C5-O1}$   $1.34(2)\text{ \AA}$ ; Scheme 1). Likewise, the  $\text{C5-C6}$  bond distance of  $1.456(5)\text{ \AA}$  in **1**, is shorter than the C–C single bond in  $\text{pd}^0$  ( $1.54(6)\text{ \AA}$ ), but longer than the C–C double bond in  $\text{pd}^{2-}$  ( $1.38(2)\text{ \AA}$ ).<sup>13</sup> These data are also in good agreement with the metrics obtained from DFT calculations (*vide infra*).

We also obtained on one occasion the solid-state molecular structure of a protonated hydroquinone decomposition product  $[\text{CoCp}_2]^+[\text{C}_{12}\text{H}_7\text{N}_2\text{O}_2]^-$  from the reaction of **1** with adventitious water. This decomposition product is crystallographically very different from **1** (see ESI†). We were unable to obtain single crystals of **3** and **4** suitable for X-ray diffraction. However, we assign the  $\text{N,N}'$ -binding mode in **3** and **4** on the basis of NMR, IR and EPR data. We see no evidence of linkage isomerism. Furthermore, the electronic spectra of **3** and **4** are well reproduced by the TD-DFT calculations (*vide infra*). We have therefore retained selectivity in binding the coordination chemistry precursor into the stronger donor  $\text{N,N}'$ -pocket, and thus directed future reactivity of this bridging ligand to the radical- $\text{O,O}'$ -pocket.

To confirm the isolated radical form of  $\text{pd}$ , we measured the EPR spectra of **1** and **3** in MeCN solution at ambient



Fig. 1 Molecular structure of **1**. One ion pair of the four crystallographically independent pairs in the unit cell shown and hydrogen atoms omitted for clarity. Thermal ellipsoids drawn at 50% probability. Selected distances ( $\text{\AA}$ ):  $\text{C5-C6}$   $1.456(5)$ ,  $\text{C5-O1}$   $1.268(4)$ ,  $\text{C6-O2}$   $1.278(4)$ ,  $\text{Co-C}(\text{Cp})$   $2.021(3)\text{--}2.034(4)$ .







Fig. 4 Overlay of the experimental (solid line) and calculated (dashed line) electronic absorption spectra for **1** (top) and **3** (bottom) recorded at ambient temperature in MeCN. Vertical bars represent individual calculated transitions. Inset orbitals depict the donor/acceptor molecular orbitals (MO) that constitute the band at 558 nm in **1** and 639 nm in **3**.

SOMO  $\rightarrow$  LUMO+1 excitations, respectively (Fig. S22, ESI<sup>†</sup>); the latter MOs are shown in the inset in Fig. 4. The analogous bands in **3** are calculated at 405 and 567 nm, respectively (Fig. 4). These are also assigned as  $\pi \rightarrow \pi^*$  transitions within the  $\text{pd}^{\bullet-}$ , although in this instance as the organic radical is coordinated to a metal ion, they are specified as intraligand charge transfer (ILCT) transitions. Analysis of the donor and acceptor MOs shows the band at 567 is the SOMO  $\rightarrow$  LUMO+4 excitation, shown in the inset of Fig. 4. The higher energy band at 405 nm is predominantly a HOMO-2  $\rightarrow$  LUMO transition (Fig. S23, ESI<sup>†</sup>); the order is different to **1** as it includes contributions from the  $[\text{Y}(\text{hfac})_3]$  moiety. Again, the intensity of these two transitions is nicely reproduced by the TD-DFT calculations. These transitions are diagnostic of the singly-reduced radical  $\text{pd}^{\bullet-}$ ,<sup>17-19</sup> as also observed for related 9,10-phenanthroline-semiquinone ( $\text{pq}^{\bullet-}$ ) complexes  $[\text{MX}(\text{pq}^{\bullet-})(\text{PPh}_3)_2(\text{CO})]$  ( $\text{M} = \text{Ru}$ ,  $\text{X} = \text{Cl}$ ;  $\text{M} = \text{Os}$ ,  $\text{X} = \text{Br}$ ) where the dominant feature is also assigned as a  $\pi \rightarrow \pi^*$  ILCT.<sup>21,22</sup>

In conclusion, this work represents the discovery and success of a novel approach to the synthesis of rare earth-transition

metal complexes. The stability of the bridging  $\text{pd}^{\bullet-}$  ligand, and the selectivity of  $N,N'$ -binding for  $\text{Y}(\text{III})$  have been demonstrated. It is anticipated that compounds **1-4** will be useful synthons in pursuit of mixed-metal radical-bridged f-element complexes in the future.

The authors acknowledge the EPSRC (EP/L504786/1 and EP/M508056/1) and the University of Glasgow for funding. We also acknowledge the EPSRC UK National Crystallography Service at the University of Southampton.

## Conflicts of interest

There are no conflicts to declare.

## Notes and references

- 1 D. Astruc, *Electron Transfer and Radical Processes in Transition-Metal Chemistry*, Wiley VCH, 1995.
- 2 P. J. Chirik and K. Wieghardt, *Science*, 2010, **327**, 794–795.
- 3 N. H. Anderson, S. O. Odoh, Y. Yao, U. J. Williams, B. A. Schaefer, J. J. Kiernicki, A. J. Lewis, M. D. Goshert, P. E. Fanwick, E. J. Schelter, J. R. Walensky, L. Gagliardi and S. C. Bart, *Nat. Chem.*, 2014, **6**, 919.
- 4 M. Murugesu and E. J. Schelter, *Inorg. Chem.*, 2016, **55**, 9951–9953.
- 5 P. L. Arnold and Z. R. Turner, *Nat. Rev. Chem.*, 2017, **1**, 0002.
- 6 H. S. L. Pierre and K. Meyer, in *Prog. Inorg. Chem.*, ed. K. D. Karlin, 2014, vol. 58, pp. 303–416.
- 7 W. J. Evans, M. Fang, J. E. Bates, F. Furche, J. W. Ziller, M. D. Kiesz and J. I. Zink, *Nat. Chem.*, 2010, **2**, 644.
- 8 S. Demir, L.-R. Jeon, J. R. Long and T. D. Harris, *Coord. Chem. Rev.*, 2015, **289–290**, 149–176.
- 9 G. A. Fox, S. Bhattacharya and C. G. Pierpont, *Inorg. Chem.*, 1991, **30**, 2895–2899.
- 10 A. Y. Girgis, Y. S. Sohn and A. L. Balch, *Inorg. Chem.*, 1975, **14**, 2327–2331.
- 11 F. Calderazzo, F. Marchetti, G. Pampaloni and V. Passarelli, *J. Chem. Soc., Dalton Trans.*, 1999, 4389–4396.
- 12 N. M. Shavaleev, L. P. Moorcraft, S. J. A. Pope, Z. R. Bell, S. Faulkner and M. D. Ward, *Chem. Commun.*, 2003, 1134–1135.
- 13 J. R. Hickson, S. J. Horsewill, C. Bamforth, J. McGuire, C. Wilson, S. Sproules and J. H. Farnaby, *Dalton Trans.*, 2018, **47**, 10692–10701.
- 14 E. K. Brechin, L. Calucci, U. Englert, L. Margheriti, G. Pampaloni, C. Pinzino and A. Prescimone, *Inorg. Chim. Acta*, 2008, **361**, 2375–2384.
- 15 F. Calderazzo, G. Pampaloni and V. Passarelli, *Inorg. Chim. Acta*, 2002, **330**, 136–142.
- 16 C. G. Pierpont and C. W. Lange, in *Prog. Inorg. Chem.*, 2007, pp. 331–442.
- 17 D. M. Murphy, K. McNamara, P. Richardson, V. Sanchez-Romaguera, R. E. P. Winpenny and L. J. Yellowlees, *Inorg. Chim. Acta*, 2011, **374**, 435–441.
- 18 H. Bock and P. Hänel, *Z. Naturforsch. B*, 1992, **47**, 288.
- 19 S. Berger, J. Fiedler, R. Reinhardt and W. Kaim, *Inorg. Chem.*, 2004, **43**, 1530–1538.
- 20 S. Sproules and K. Wieghardt, *Coord. Chem. Rev.*, 2011, **255**, 837–860.
- 21 M. K. Biswas, S. C. Patra, A. N. Maity, S.-C. Ke, N. D. Adhikary and P. Ghosh, *Inorg. Chem.*, 2012, **51**, 6687–6699.
- 22 M. K. Biswas, S. C. Patra, A. N. Maity, S.-C. Ke, T. Weyhermüller and P. Ghosh, *Dalton Trans.*, 2013, **42**, 6538–6552.

