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

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Reduction of 1,10-phenanthroline-5,6-dione (pd) with CoCp^{R}_2 resulted in the first molecular compounds of the $\text{pd}^{\cdot-}$ semi-quinone radical anion, $[\text{CoCp}^{\text{R}}_2]^+[\text{pd}]^{\cdot-}$ (R = H, (1); R = Me₄, (2)). Furthermore compounds 1 and 2 were reacted with $[\text{Y}(\text{hfac})_3(\text{thf})_2]$ (hfac = 1,1,1-5,5,5-hexafluoroacetylacetonate) to synthesise the rare earth-transition metal heterometallic compounds, $[\text{CoCp}^{\text{R}}_2]^+[\text{Y}(\text{hfac})_3(\text{N,N}'\text{-pd})]^{\cdot-}$ (R = H, (3); R = Me₄, (4)).

Electron transfer reactions are fundamental to chemical processes. Stable organic and organometallic radicals are widely utilised, particularly in small molecule activation and catalysis.¹ 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 metals² and has also been demonstrated for the f-elements.^{3,4}

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.* $\text{CO}^{\cdot-}$, $\text{CO}_2^{\cdot-}$ and $\text{NO}^{\cdot-}$.⁵⁻⁷ 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.^{4,8} 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

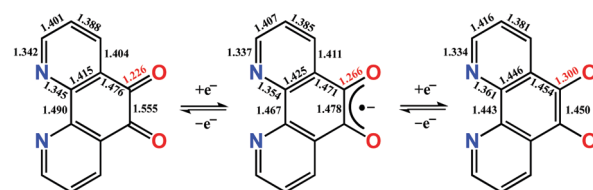
bridging ligands used in f-element chemistry have identical binding sites that lead near exclusively to homobimetallic complexes.

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 π -accepting diimine unit analogous to 2,2'-bipyridine, and distinct from the O,O'-pocket which is a π -donating diolate, akin to a catecholate.

There is literature precedent for the formation of multi-metallic complexes using the dianionic form of the ligand.⁹⁻¹² We also recently reported heterometallic rare earth-transition metal complexes utilising pd as a template.¹³ 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.^{11,14,15}

In contrast to the well-developed chemistry of transition metal semiquinones,¹⁶ there are only three reports of the *in situ* characterisation of $\text{pd}^{\cdot-}$.¹⁷⁻¹⁹ 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, $[\text{CoCp}^{\text{R}}_2]^+[\text{pd}]^{\cdot-}$ (R = H, (1); R = Me₄, (2)).



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

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

Furthermore, we demonstrate the coordination chemistry of **1** and **2**, with $[Y(hfac)_3(thf)_2]$ ($hfac = 1,1,1-5,5,5$ -hexafluoroacetylacetonate) to synthesise the rare earth-transition metal heterometallic compounds, $[CoCpR_2]^+[Y(hfac)_3(N,N'-pd)]^{\bullet-}$ ($R = H$, (**3**); $R = Me_4$, (**4**)). Our first choice of synthon for this chemistry was the potassium salt of $pd^{\bullet-}$, formed by reduction of pd with KH (see ESI†). However, while the spectroscopic data are consistent with $[K]^+[pd]^{\bullet-}$, its synthetic utility is limited. The reductants $CoCpR_2$ 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 $CoCpR_2$ to a suspension of 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 $CoCp^t_2$ being generated *in situ*. The subsequent addition of a solution of $[Y(hfac)_3(thf)_2]$ to a solution of either **1** (RT) or **2** ($-35\text{ }^\circ\text{C}$) 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 1H NMR spectra of **1** and **2** in d_3 -MeCN at room temperature are consistent with $[CoCpR_2]^+$ and display no other resonances. In addition to the $[CoCpR_2]^+$ resonances, the 1H NMR spectra of **3** in d_3 -MeCN and **4** in d_8 -THF at room temperature display both broadened proton environments in the $pd^{\bullet-}$ region and $hfac$ singlets (this latter in the appropriate ratio for the 1 : 1 adduct). These data are consistent with remote *i.e.* N,N' -binding to $pd^{\bullet-}$. The ATR IR spectra of **1** and **2** are also consistent with the reduction of pd to $pd^{\bullet-}$. The ν_{CO} of neutral pd of 1678 cm^{-1} is no longer visible and there are two strong absorptions in the expected range for semiquinone radicals (1500 – 1400 cm^{-1}) at 1511 cm^{-1} and 1485 cm^{-1} .^{11,15} The ATR IR spectrum of $[K(DME)_x]^+[pd]^{\bullet-}$ ($DME = \text{dimethoxyethane}$, see ESI†), which does not contain aromatic ν_{CC} also displays two strong absorptions at 1518 cm^{-1} and 1504 cm^{-1} . We therefore assign both absorptions in **1** and **2**, centred *ca.* 1500 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 $hfac$ also occur in the same region. There are no absorptions in catecholate region, consistent with N,N' -binding. Electronic spectra of **1**–**4** were collected in MeCN or THF (see ESI†) and

are consistent with electrochemically generated $pd^{\bullet-}$.^{17–19} 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 $-35\text{ }^\circ\text{C}$, 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 $pd^{\bullet-}$. The metrics important for assessing the redox state of the ligand are those of the O,O' -pocket. In particular the bond distances of $C5-O1$ $1.268(4)\text{ \AA}$ and $C6-O2$ $1.278(4)\text{ \AA}$ in **1** are identical within error to one another and intermediate in length between a C–O double bond (pd^0 , $C6-O2$ $1.23(2)$ and $C5-O1$ $1.24(2)\text{ \AA}$) and a C–O single bond (pd^{2-} , $C6-O2$ $1.35(1)$ and $C5-O1$ $1.34(2)\text{ \AA}$; Scheme 1). Likewise, the $C5-C6$ bond distance of $1.456(5)\text{ \AA}$ in **1**, is shorter than the C–C single bond in pd^0 ($1.54(6)\text{ \AA}$), but longer than the C–C double bond in pd^{2-} ($1.38(2)\text{ \AA}$).¹³ 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 $[CoCp_2]^+[C_{12}H_7N_2O_2]^-$ 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 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 N,N' -pocket, and thus directed future reactivity of this bridging ligand to the radical- O,O' -pocket.

To confirm the isolated radical form of 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 (\AA): $C5-C6$ $1.456(5)$, $C5-O1$ $1.268(4)$, $C6-O2$ $1.278(4)$, $Co-C(Cp)$ $2.021(3)$ – $2.034(4)$.





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[†]); 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[†]); 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 $\text{pd}^{\bullet-}$,¹⁷⁻¹⁹ 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.^{21,22}

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.

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Conflicts of interest

There are no conflicts to declare.

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