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COMMUNICATION

A new fluorone-based bridging ligand for discrete and polymeric assemblies including Mo and W based [4+4] metallocycles

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Redox-active ligands are of interest for their ability to link metal centres and generate electroactive materials. We report the synthesis of 9-hydrogen-2,3,7-trihydroxyfluorone, which is able to serve as a bridging ligand and has the potential to exist in multiple oxidation states. Anionic [4+4] metallocycles in which Mo or W centres are linked by the trianion of this ligand are also described.

Redox-active bridging ligands have attracted significant attention due to their ability to enable mixed-valency within coordination polymers, which can result in unusual electronic and/or magnetic properties.[1-6] The dianions of 2,5-dihydroxy-1,4-benzoquinone (H_2dhbq) and related compounds such as chloranilic acid are perhaps one of the most extensively studied class of ligands and are known to form mixed-valency coordination polymers.[7-14] These planar organic anions which possess delocalised π-systems are not only redox-active (see Fig. 1), but also allow for the assembly of a variety of high symmetry 2- and 3- dimensional networks.[15-17]

Upon deprotonation, the tricyclic 2,3,7-trihydroxyfluorones, exhibit similarities with dhbq^{2-} in that they are able to bridge and chelate metal centres and are capable of existing in multiple oxidation states (Fig. 2). An appealing feature of the fluorone family is the relative synthetic ease in which the backbone may be functionalised at the 9-position.[18, 19] A long-term goal of our group has been to synthesise and investigate the electronic properties of frameworks formed with such ligands.

Whilst 2,3,7-trihydroxyfluorones have been extensively used for analytical purposes, there have been relatively few structurally characterised metal complexes. Several dinuclear complexes, in which metal centres are bridged by 9-phenyl-2,3,7-trihydroxyfluorone, have been reported and have displayed interesting magnetic and spectro-electronic properties.[20-25] In 2014, we reported a series of discrete anionic [4+4] Mo and W-based metallocycles with this ligand.[26]

We have now turned our attention to a simpler fluorone, namely, 9-hydrogen-2,3,7-trihydroxylfluorone because it offers the prospect of generating both discrete and infinite supramolecular assemblies with a reduced steric profile. We report here a synthetic approach for the generation of 9-hydrogen-2,3,7-trihydroxyfluorone and describe a series [4+4] Mo- and W-based metallocycles as part of an initial structural exploration of the ligand.

Although a wide variety of 2,3,7-trihydroxyfluorones,with various substituents at the 9-position have been described,[27] to the best of our knowledge, a synthesis for 9-hydrogen-2,3,7-trihydroxyfluorone has not been reported. A typical route for preparation of these compounds involves the reaction of 1,2,4-triacetoxybenzene with an aromatic aldehyde under acidic conditions, followed by oxidation. In an adaptation of this approach, reactions with formaldehyde were performed, however, these reactions yielded 9-methyl-2,3,7-trihydroxyfluorone. We suspect that the cleavage of the acetoxy groups (of the 1,2,4-triacetoxybenzene under acidic conditions) generated significant amounts of acetaldehyde whose incorporation was favoured in the formation of the resultant fluorone.

A large stoichiometric excess of formic acid, in place of the typical aldehyde ultimately yielded the desired product, 9-hydrogen-2,3,7-trihydroxyfluorone (detailed synthetic information is available in the ESI).

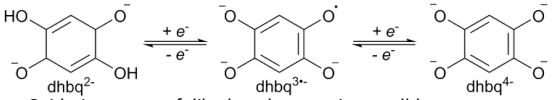

Fig. 1 Oxidation states of dihydroxybenzoquinone, dhbq.

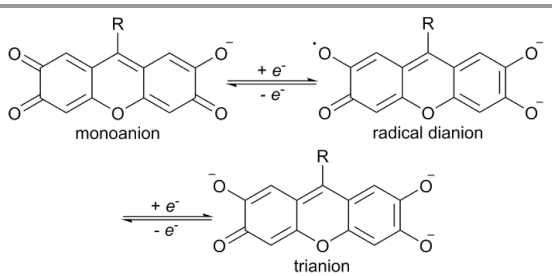

Fig. 2 Potential oxidation states of 9-subsituted-2,3,7-trihydroxyfluorones. Note that additional resonance forms exist for each anion.

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Electronic Supplementary Information (ESI) available: [Details of synthetic procedures, powder diffraction patterns, NMR spectra and further crystallographic details; CCDC reference numbers: 2003523-2003526]. See DOI: 10.1039/x0xx00000x

Following the successful synthesis of 9-hydrogen-2,3,7-trihydroxyfluorone, we investigated its ability to bridge metal centres and form large metallocycles. A longer term aim is to use these ligands to generate redox-active coordination networks. Reactions of the hydrochloride salt of 9-hydrogen-2,3,7-trihydroxfluorone with Na_2MO_4 (M = Mo or W) and XPh_4^+ (X = P or As) in aqueous methanol under solvothermal conditions yielded red rod-like crystals with a green iridescence.

Crystallographic analyses revealed the four compounds crystallise in the tetragonal class with cell dimensions a ≈ 30 Å and c ≈ 15 Å.‡ Structure determinations in enantiomeric space groups, either $P4_32_12$ or $P4_12_12$, revealed a series of compounds with the general formula; $(XPh_4)_4[(MO_2)_4(9HL)_4]$ (X = P or As, M = Mo or W). The four compounds are essentially isostructural, with minor differences arising from the different metal centres and/or charge-balancing cations.

The discrete anionic $[(MO_2)_4(9HL)_4]^{4-}$ (M = Mo or W) square-like [4+4] metallocycles are comprised of two crystallographically distinct 9-hydrogen-2,3,7-trihydroxy-fluorone ligands and three crystallographically distinct metal centres (Fig. 3a). Bond valence sum analysis for each metal centre is consistent with a +6 oxidation state (see ESI). The metal sites, M1 and M3, lie on a two-fold axis which bisects the metallocycle. The metal centres are chelated by a pair of bridging fluorone units, with an M···M distance of ~12.8 Å. The internal angles of the 'square' metallocycle deviate from 90° with acute and obtuse angles in the ranges 83.5 – 84.2° and 96.0 – 96.5° respectively. Terminal *cis*-oxo groups occupy the remaining coordination sites of a distorted octahedral coordination geometry.

Carbon-oxygen bond lengths along the C9/H9 edge (Fig. 4) are similar to that found in catechol (~1.35 Å), whilst along the xanthene edge the C-O bonds are significantly shorter (~1.29 Å). The observed bond lengths are consistent with those observed in other 2,3,7-trihydroxyfluorone based systems (see ESI), and the assignment of the carbon atom in the C-9 position. Bond lengths along the xanthene edge are in accordance with the resonance forms expected for the trianion (Fig. 2).

Within the anionic squares, each fluorone ligand is inclined by ~54° to the mean plane of the metal centres, with both the C-9 and H-9 atoms oriented away from the square. Thus, the C-9 side of each ligand alternates above and below the mean plane of the square. Earlier work with the 9-phenyl-2,3,7-trihydroxyfluorone suggested that the sterically bulky phenyl group was responsible for the xanthene edge being directed towards the centre of the square. However, in this system with the H atom in the 9-position, steric factors play a less important role. Inspection of Fig. 3 reveals that the oxygen atom from the xanthene edge is *trans* to an oxo group whereas the O donors from the C9/H9 edge are *cis* to both oxo groups. This arrangement may reflect a preferred coordination configuration at the metal centre in which the stronger donor O atoms, each formally carrying a full negative charge as indicated in Fig. 2, prefer to be *cis* to the oxo substituents.

The metal centres alternate in configuration within a metallocycle i.e. Δ, Λ, Δ, Λ. This alternation is crucial in the formation of the squares - if all metal centres possessed the same stereo-configuration a 1D helix would form. The most symmetric idealised conformation of a metallocycle has an achiral point group symmetry of D_{2d}. However, a less symmetric

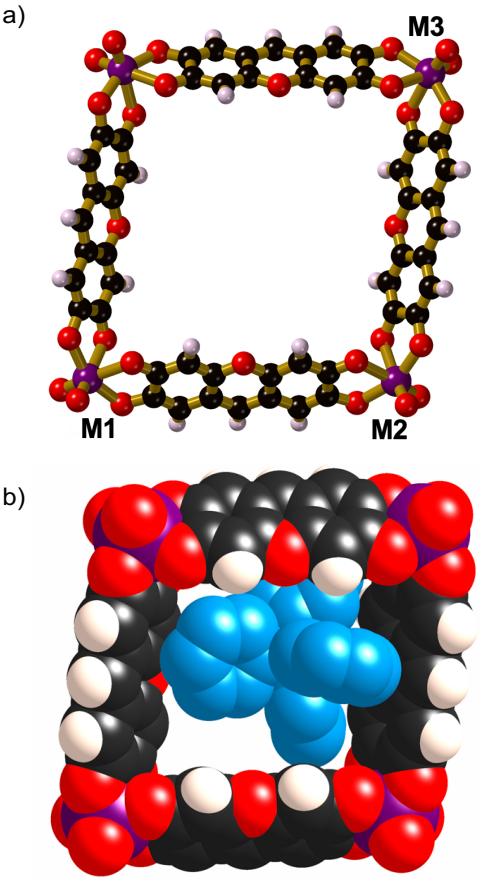

Fig. 3 The $[(MoO_2)_4(9HL)_4]^{4-}$ metallocycle from $(PPh_4)_4[(MoO_2)_4(9HL)_4]$ represented in a) ball and stick form with the crystallographic unique metal sites labelled; a two-fold axis runs through metal sites M1 and M3 and b) space-filling form showing the of the PPh_4^+(blue) inside the metallocycle; only one of the two orientations of the phenyl groups is shown.

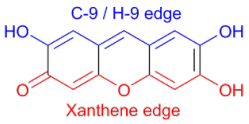

Fig. 4 The 9-hydrogen-2,3,7-trihydrofluorone molecule with the C-9/H-9 edge and xanthene edges indicated.

conformation, which is chiral, is adopted in the solid-state. With the complexes crystallising in a chiral space group, either $P4_12_12$ or $P4_32_12$, all squares within a crystal are the same enantiomer. The bulk product is expected to exist as a racemic mixture of crystals.

The negative charge associated with each $[(MO_2)_4(9HL)_4]^{4-}$ (M = Mo or W) metallocycle is balanced by four cations. In the compounds reported herein these are sterically bulky species; PPh_4^+ or $AsPh_4^+$. Within each of these compounds, there are three crystallographically unique cations – two of which are located on 2-fold axes. A disordered cation sits within the cavity of each metallocycle, and forms both close edge-to-face and face-to-face interactions with the 9-hydrogen-2,3,7-trihydroxyfluorone ligand (shortest contacts ~3.4 Å) (Fig. 3b)

Anionic metallocycle squares stack in the *c*-direction and interleave with a neighbouring stack to form a double stack as

indicated in (Fig. 5). Parallel double stacks, in two different orientations, run parallel with the *c*-axis. The corners that overlap to form a double stack are the same corners occupied by XPh_4^+ cations (X = As, P) as depicted in Fig. 3b. These cations play a key structural role in regard to the formation of the interleaved double stacks. In addition to the association between the XPh_4^+ and the host metallocycle (Fig. 3b) the cation interacts with MO_2 (M = Mo or W) cores of neighbouring anionic squares located directly above and below (Fig. S3.1). The remaining two crystallographically unique types of cations reside in between neighbouring squares.

Solvent molecules, methanol and/or water, occupy interstitial spaces within the crystal packing. Estimations of the solvent occupied space are between 7 and 11% (see ESI).

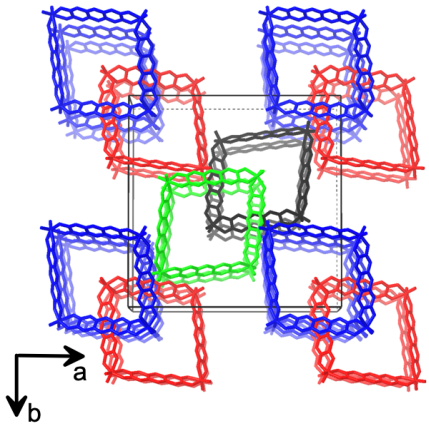

Fig. 5 Crystal packing of the $[(MoO_2)_4(9HL)_4]^{4-}$ squares within $(PPh_4)_4[(MoO_2)_4(9HL)_4$ viewed along the *c* axis. The black and green metallocycles form an interleaved double stack. The red and blue stacks are symmetry related to the black and green but have a different orientation.

In summary, the successful synthesis of 9-hydrogen-2,3,7-trihydroxyfluorone has been achieved and its intended use as a bridging ligand in its trianionic form has been demonstrated. The formation of the [4+4] metallocycles, in which either *cis*-dioxo-Mo(VI) or -W(VI) centres are able to bind to two chelating ligands, provides encouragement that the ligand will be able to bridge metal centres within porous network materials, with metal to metal separations approaching 13 Å. This compares to a separation of ~8 Å in the case of the bridging chloranilate ligand. In regards to such materials, the presence of relatively large channels, which may be expected to result from the use of such a long bridging ligand, offers scope for introducing a range of guests, such as oxidants, into a coordination network. Chemical or electrochemical oxidation of the ligand to a monoanion or a radical dianion within the network would appear to be a reasonable proposition. The electronic and magnetic properties of such materials, especially when paramagnetic metal centres and/or redox active metal centres are employed, would certainly be worthy of investigation.

Conflicts of interest

There are no conflicts to declare.

Acknowledgments

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Notes and references

‡ Crystal data for $(PPh_4)_4[(MoO_2)_4(9HL)_4]\cdot 4MeOH\cdot 3H_2O$: $C_{152}H_{122}Mo_4O_{35}P_4$, M = 3016.13, tetragonal, a = 30.160(4) Å, c = 14.716(3) Å, U = 13386(5) Å^3, T = 100.0(1) K, space group $P4_32_12$ (no. 96), Z = 4, 120107 reflections measured, 9268 unique (R_{int} = 0.1490), which were used in all calculations. The final $wR(F^2)$ was 0.1694 (all data) and $R1$ [$I > 2\sigma(I)$] was 0.0745, Flack parameter = -0.025(16). Crystal data for $(PPh_4)_4[(WO_2)_4(9HL)_4]\cdot 4MeOH\cdot 3H_2O$: $C_{152}H_{122}O_{35}P_4W_4$, M = 3367.77, tetragonal, a = 30.2142(2) Å, c = 14.7473(2) Å, U = 13462.8(3) Å^3, T = 100.0(1) K, space group $P4_32_12$ (no. 96), Z = 4, 47975 reflections measured, 13947 unique (R_{int} = 0.0443), which were used in all calculations. The final $wR(F^2)$ was 0.1051 (all data) and $R1$ [$I > 2\sigma(I)$] was 0.0406, Flack parameter = -0.024(5). Crystal data for $(AsPh_4)_4[(MoO_2)_4(9HL)_4]\cdot 3MeOH\cdot 4H_2O$: $C_{151}H_{120}As_4Mo_4O_{35}$, M = 3177.90, tetragonal, a = 30.135(4) Å, c = 14.809(3) Å, U = 13448(4) Å^3, T = 100(2) K, space group $P4_32_12$ (no. 96), Z = 4, 228684 reflections measured, 16126 unique (R_{int} = 0.0713), which were used in all calculations. The final $wR(F^2)$ was 0.1191 (all data) and $R1$ [$I > 2\sigma(I)$] was 0.0470, Flack parameter = 0.018(2). Crystal data for $(AsPh_4)_4[(WO_2)_4(9HL)_4]\cdot 4MeOH\cdot 4H_2O$: $C_{152}H_{124}As_4O_{36}W_4$, M = 3561.58, tetragonal, a = 30.3905(3) Å, c = 14.8757(2) Å, U = 13738.9(3) Å^3, T = 130.0(1) K, space group $P4_12_12$ (no. 92), Z = 4, 27926 reflections measured, 12316 unique (R_{int} = 0.0257), which were used in all calculations. The final $wR(F^2)$ was 0.0980 (all data) and $R1$ [$I > 2\sigma(I)$] was 0.0428, Flack parameter = -0.021(4).

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