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Polyoxometalates

Guest Editors: De-Liang Long and Leroy Cronin

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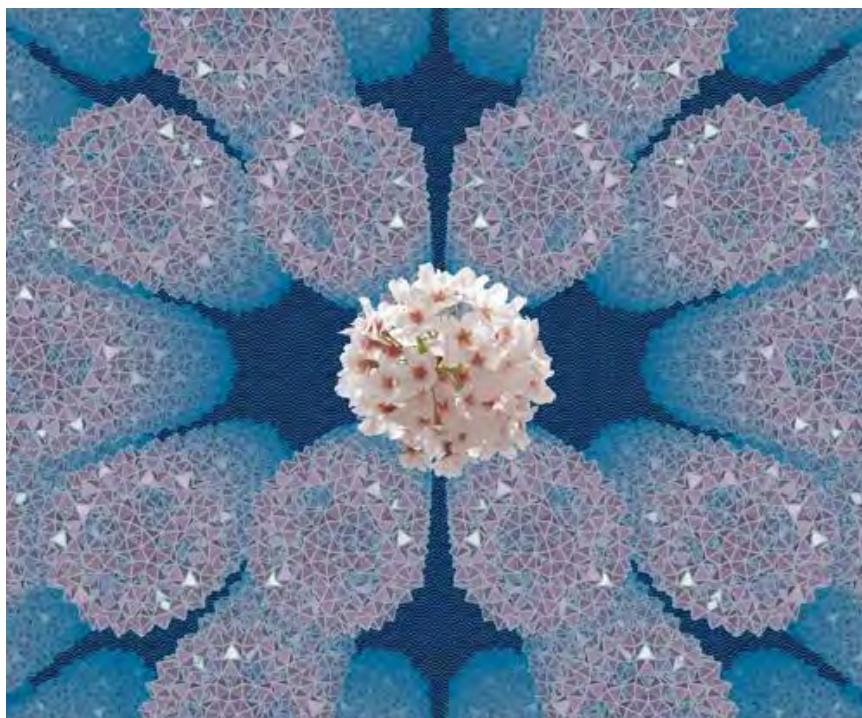


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PAPER

Organic-soluble lacunary $\{M_2(P_2W_{15}O_{56})_2\}$ polyoxometalate sandwiches showing a previously unseen $\alpha\beta\alpha$ isomerism†

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New polyoxometalate ‘sandwiches’ have been formed where two $[P_2W_{15}O_{56}]^{12-}$ lacunary Dawson clusters encapsulate two transition metal ions to give clusters with the general formula $[M^{II}_2(P_2W_{15}O_{56})_2]^{20-}$ (where M = Mn, Co, and Ni respectively), $[Fe^{III}_2(P_2W_{15}O_{56})_2]^{18-}$, and $[Cu^{II}_4(P_2W_{15}O_{56})_2]^{16-}$. The Mn, Co, and Ni clusters exhibit a hitherto unseen $\alpha\beta\alpha$ isomeric geometry and all five compounds are associated with tetrabutylammonium cations which allow for their dissolution in non-aqueous solvent.

Introduction

Polyoxometalates (POMs) are a vast and varied class of molecular metal oxide clusters formed from early transition metal cations in their highest oxidation state linked by shared oxo ligands.^{1–3} These anionic clusters are assembled *via* condensation reactions in acidic solution⁴ and can be partially disassembled in controlled basic conditions giving lacunary POMs which have vacancies in their structure⁵ (as opposed to plenary POMs which have no vacant sites). Lacunary POMs can be reacted further with other transition metal species in acidic solution to form structures where the vacant sites are occupied by the new transition metal ion.^{6,7} Reactions of this type have allowed the substitution of most d-block elements into POM structures to give new polyoxometalates with emergent properties.^{8–11}

The trivacant lacunary POM $[P_2W_{15}O_{56}]^{12-}$ (shortened to $\{P_2W_{15}\}$) is formed by controlled decomposition of the parent phosphotungstic Dawson¹² anion $[P_2W_{18}O_{62}]^{6-}$ to remove a triad of tungsten atoms located at one polar ‘cap’ of the cluster.^{13–15} This trivacant POM is known to combine with a variety of transition metal ions to give two types of structurally unique compounds. First, with high valent transition metal ions such as Mo^{VI} , W^{VI} , V^V , Nb^V and Ta^V the incoming metals refill the vacant cap positions giving compounds of general formula $[M_3P_2W_{15}O_{62}]^{n-}$, where M is the new metal.^{16,17} However, with

lower valent metals such as Mn^{II} , Fe^{III} , Co^{II} , Ni^{II} , Cu^{II} , and Zn^{II} ‘sandwich’ compounds are formed where two of the lacunary $[P_2W_{15}O_{56}]^{12-}$ anions are joined by the sharing of transition metal ions^{18–23} (the POMs are the bread of the sandwich and the encapsulated transition metal ions are the filling). The most common architecture formed from reactions of this type is known as the Weakley sandwich which consists of a diamond arrangement of four transition metal ions encapsulated between two trilacunary POMs. This is favoured because a diamond arrangement of four transition metal ions is capable of coordinating between the three vacant metal sites on two discrete POMs (see Fig. 1).

Whilst it is possible to form Weakley-type sandwiches with fewer than four transition metal ions, these clusters are considered to still be lacunary, and in the solid state the vacant sites are usually occupied by alkali cations with coordinated water molecules. An example of a trinuclear analogue is the tricobalt sandwich reported by Thouvenot *et al.* which has a sodium cation occupying the vacancy where the fourth transition metal is commonly found.^{24,25} Examples of dinuclear sandwiches are less common but include an iron cluster,²⁶ $[(NaOH)_2-Fe^{III}_2(As_2W_{15}O_{56})_2]^{16-}$, its copper analogue²⁷ $[(NaOH)_2-Cu^{II}_2(P_2W_{15}O_{56})_2]^{18-}$, and the cobalt version²⁴ $[(NaOH)_2-Co^{II}_2(P_2W_{15}O_{56})_2]^{18-}$, all of which also contain hydrated sodium ions in the vacant sites. It has been shown that these sodium atoms can be exchanged for other metal ions to give mixed metal sandwiches,^{28,29} highlighting the increased reactivity of these species. There has been one published example of a dinuclear sandwich which does not contain any alkali metals in the lacunary sites and this is the dititanium sandwich, $[(Ti^{IV}P_2W_{15}O_{55}OH)_2]^{14-}$, which is formed as an ammonium salt.³⁰ It is possible to form different isomers of these clusters depending on the orientation of the transition metal centres in the junction. Interestingly all of these dinuclear sandwiches form the $\alpha\alpha\alpha$ isomer whereas the tetranuclear sandwiches tend to adopt the $\alpha\beta\alpha$ arrangement.³¹

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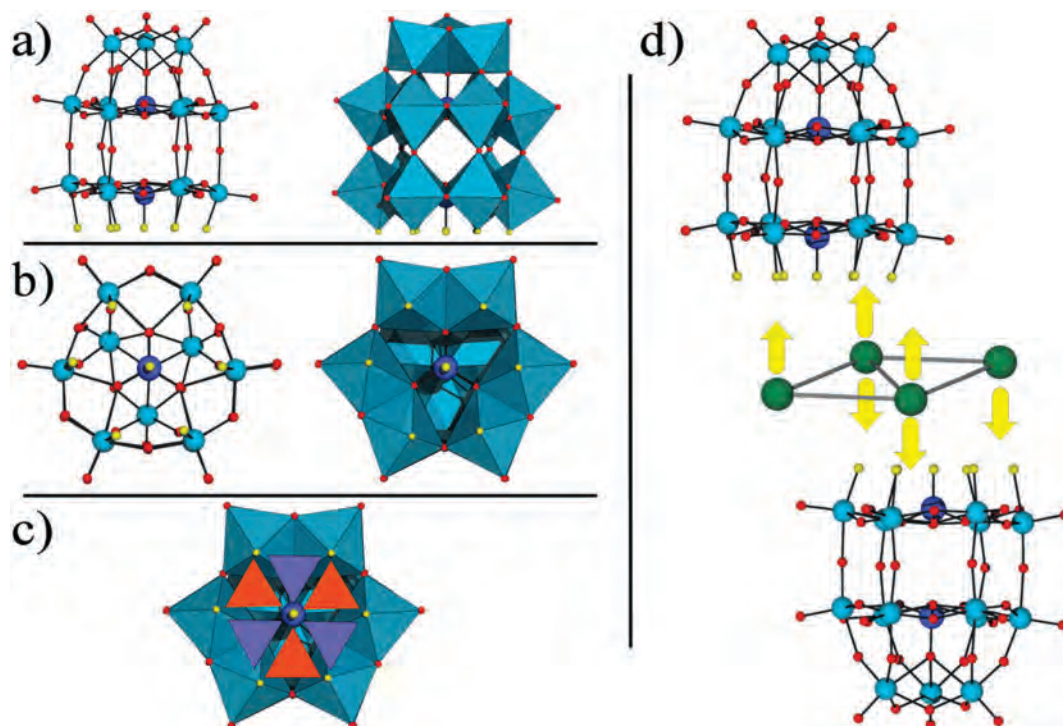


Fig. 1 (a) Left: ball and stick representation of the trivalent Dawson, $[P_2W_{15}O_{56}]^{12-}$ $\{P_2W_{15}\}$. The three vacancies are found at the bottom of the cluster and the ring of reactive oxygen atoms which bonds to the transition metal core is highlighted in yellow. Right: polyhedral representation of the same structure. (b) Ball and stick and polyhedral representation of the view from underneath the cluster. Here the ring of yellow reactive oxygen atoms is more clearly visible along with the pendant oxo ligand on the central phosphate group which also bonds to the transition metal core. (c) Diagram showing the two possible locations for the three metal centres from the core to bind. Metals which prefer a longer M–O(W) bond in the place of the purple triangles, metals which prefer shorter bonds are found where the red triangles are located. This means that it is possible to form four different isomers of each sandwich compound. (d) Showing how the tetranuclear moiety found in Weakley-type sandwiches is capable of filling the lacunary vacancies of two trivalent $\{P_2W_{15}\}$ anions (the bonds between the atoms on this moiety are non-existent and the transition metals are held together by oxo-bridges from the oxygen atoms on the lacunary POM).

Here we report a new synthetic technique which results in the isolation of tetrabutylammonium (TBA) salts of Weakley-type Dawson sandwiches from alkali POM salts in a one pot reaction. Interestingly, for the metals Mn, Fe, Co, and Ni these sandwiches contain only two metals and are stable despite the absence of alkali metals in the remaining addendum atom vacancies. The products for the metals Mn, Co, and Ni are also $\alpha\beta\alpha$ isomers and represent the first examples of this sandwich type.

Experimental

Syntheses

All chemicals and solvents were of analytical grade purchased from Sigma Aldrich and used as supplied, without further purification. $Na_{12}[\alpha-P_2W_{15}O_{56}] \cdot 24H_2O$ was synthesised by a previously reported method.³²

(TBA)₉Na[H₁₀Mn^{II}₂(P₂W₁₅O₅₆)₂] · 6CH₃CN (1). Into 50 mL of deionised water was dissolved 1.5 mmol of $MnSO_4 \cdot H_2O$ followed by $Na_{12}[\alpha-P_2W_{15}O_{56}] \cdot 24H_2O$ (1.0 g, 0.23 mmol) and the solution was stirred for 10 minutes. 75 mL of acetonitrile was then added to this reaction mixture giving a cloudy solution which was stirred for a further 5 minutes followed by the addition of tetrabutylammonium bromide (6.0 g, 18.6 mmol).

The solution was then stirred for another 10 minutes before lowering the pH to 1.5 using aqueous 4.5 M sulfuric acid. The resulting turbid solution was stirred for a further 5 minutes and then set aside for 2–3 hours. During this time an oily material was formed which separated down the beaker, and was collected by centrifugation. The aqueous solution was poured away and the oil was washed three times with 20 mL aliquots of water and once with a 20 mL aliquot of ethanol to dry (take care, the ethanol slightly dissolves the product) eventually resulting in a fine red/brown powder which was dried overnight in a desiccator. This powder is recrystallised in acetonitrile/ether diffusion affording red/brown crystals of **1** in 43.1% yield (based on W).

Elemental analysis calcd (found): Mn 1.10 (0.97), W 55.32 (55.7), Na 0.23 (0.44), C 18.79 (17.32), H 3.56 (3.35), N 2.10 (1.53).

(TBA)₈[H₁₂Co^{II}₂(P₂W₁₅O₅₆)₂] · 3CH₃CN (2). The same reaction conditions were used as for the formation of **1** except that the $MnSO_4 \cdot H_2O$ is replaced with an equimolar amount of $CoSO_4 \cdot 7H_2O$ to give red crystals of **2** in 39.3% yield.

Elemental analysis calcd (found): Co 1.22 (1.01), W 57.30 (59.7), C 16.72 (16.48), H 3.24 (3.22), N 1.60 (1.49).

(TBA)₉[H₁₁Ni^{II}₂(P₂W₁₅O₅₆)₂] · CH₃CN (3). The same reaction conditions were used as for the formation of **1** except that the

MnSO₄·H₂O is replaced with an equimolar amount of NiSO₄·6H₂O to produce raw materials of **3** in 87% yield.

Elemental analysis calcd (found): Ni 1.21 (0.58), W 57.01 (60.45), C 17.01 (18.05), H 3.50 (3.47), N 1.45 (1.68).

(TBA)₈Na[H₉Fe^{III}₂(P₂W₁₅O₅₆)₂]-2CH₃CN (**4**). The same reaction conditions were used as for the formation of **1** except that the MnSO₄·H₂O is replaced with an equimolar amount of FeSO₄·7H₂O to give yellow crystals of **4** in 45.2% yield.

Elemental analysis calcd (found): Fe 1.16 (1.65), W 57.47 (60.8), Na 0.24 (0.3), C 16.52 (16.68), H 3.18 (3.22), N 1.45 (1.42).

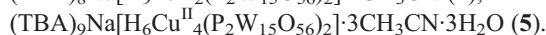
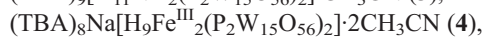
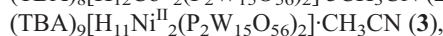
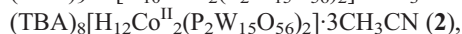
(TBA)₉Na[H₆Cu^{II}₄(P₂W₁₅O₅₆)₂]-3CH₃CN·3H₂O (**5**). The same reaction conditions were used as for the formation of **1** except that the MnSO₄·H₂O is replaced with an equimolar amount of CuSO₄·5H₂O to give yellow/green crystals of **5** in 53.8% yield.

Elemental analysis calcd (found): Cu 2.52 (1.66), W 54.74 (60.9), Na 0.23 (0), C 17.88 (17.71), H 3.45 (3.42), N 1.67 (1.88).

Results and discussion

Syntheses and structure

The reaction proceeds by first dissolving the alkali salt of the {P₂W₁₅} anion and the required transition metal sulfate in water, followed by the addition of a larger volume of acetonitrile (by 3 : 2). This produces a cloudy solution to which is added an excess of TBA bromide and this solution is acidified to pH 1.5 with sulfuric acid giving a slightly turbid solution which eventually produces oil that settles to the bottom of the reaction vessel. This oil can be extracted and washed with water to give a powdered product which can be recrystallised in an acetonitrile/diethyl-ether diffusion. This reaction was performed with the transition metal sulfates of Mn, Fe, Co, Ni, and Cu to give the compounds:



All five compounds have been characterised using X-ray single crystal structure determinations, crystal data of which are listed in Table 1. As shown in Fig. 2 compounds **1–4** are dinuclear sandwiches containing two transition metal ions whilst compound **5** is a tetranuclear copper sandwich. All except compound **4** contain the transition metal in the +2 oxidation state. The compounds are all formed as a mixed TBA/proton salt with slight alkali metal impurity in compounds **1**, **4**, and **5**.

The majority of the cations on all of these compounds are TBA and protons. The TBA cation was employed due to its large size and low polarity. The large steric size of this cation is capable of directing the assembly of POMs into more reactive lacunary arrangements by hindering the formation of larger plenary structures.^{33,34} The low polarity of this compound allows clusters with this cation to be dissolved in solvents with lower polarity than water, for example, acetonitrile, allowing the cluster to be used for catalysis in organic media,^{35,36} for further

Table 1 Crystal data for compounds **1–5**

Identification code	1	2	3	4	5
Empirical formula	C ₁₅₀ H ₃₃₂ Mn ₂ Ni ₁₅ NaO ₁₁₂ P ₄ W ₃₀	C ₁₅₄ H ₃₀₉ Co ₂ Ni ₁₁ O ₁₁₂ P ₄ W ₃₀	C ₁₄₆ H ₃₃₈ Ni ₁₀ Ni ₂ O ₁₁₂ P ₄ W ₃₀	C ₁₃₂ H ₃₀₃ Fe ₂ Ni ₁₀ NaO ₁₁₂ P ₄ W ₃₀	C ₁₅₀ H ₃₄₅ Cu ₄ Ni ₁₂ NaO ₁₁₂ P ₄ W ₃₀
Formula weight (g mol ⁻¹)	10002.78	9624.16	9783.06	9596.91	10073.91
Temperature (K)	150(2)	150(2)	150(2)	150(2)	150(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 1	<i>C</i> 2/c	<i>C</i> 2/c	<i>C</i> 2/c	<i>C</i> 2/c
<i>a</i> (Å)	15.4501(2)	29.5229(5)	45.2790(9)	47.3357(16)	35.5081(16)
<i>b</i> (Å)	19.6621(4)	29.3096(4)	21.0927(7)	17.9304(6)	15.7651(6)
<i>c</i> (Å)	28.1389(5)	30.8213(5)	31.0661(11)	38.5281(11)	48.504(3)
<i>α</i> (°)	70.288(2)	90	90	90	90
<i>β</i> (°)	89.395(2)	100.074(2)	97.190(6)	114.472(2)	90.826(5)
<i>γ</i> (°)	67.700(2)	90	90	90	90
Volume (Å ³)	7377.3(2)	262.58(6(7))	29436.6(15)	29762.9(17)	27149(2)
<i>Z</i>	1	4	4	4	4
Density (calculated)	2.251 Mg m ⁻³	2.434 Mg m ⁻³	2.207 Mg m ⁻³	2.142 Mg m ⁻³	2.465 Mg m ⁻³
Absorption coefficient (mm ⁻¹)	11.817	25.371	11.883	22.303	23.990
<i>F</i> (000)	4630	17 680	18 064	17 616	18 624
Crystal size (mm ³)	0.46 × 0.21 × 0.10	0.35 × 0.28 × 0.23	0.35 × 0.19 × 0.07	0.27 × 0.26 × 0.24	0.17 × 0.07 × 0.06
Reflections collected	146 141	96 962	87 247	66 530	42 551
Independent reflections (<i>R</i> _{int})	28 945 (0.0370)	23 716 (0.0687)	17 953 (0.1196)	19 143 (0.1477)	19 321 (0.1036)
Data/restraints/parameters	28 945/87/1425	23 716/40/922	17 953/48/811	19 143/63/917	19 321/23/911
Goodness-of-fit on <i>F</i> ²	1.081	1.022	0.895	1.126	0.993
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] <i>R</i> ₁ , <i>wR</i> ₂	0.0349, 0.1029	0.0807, 0.2014	0.0783, 0.1977	0.1065, 0.3115	0.0928, 0.2491
<i>R</i> indices (all data) <i>R</i> ₁ , <i>wR</i> ₂	0.0421, 0.1075	0.0886, 0.2114	0.1807, 0.2286	0.1368, 0.3387	0.1503, 0.2896

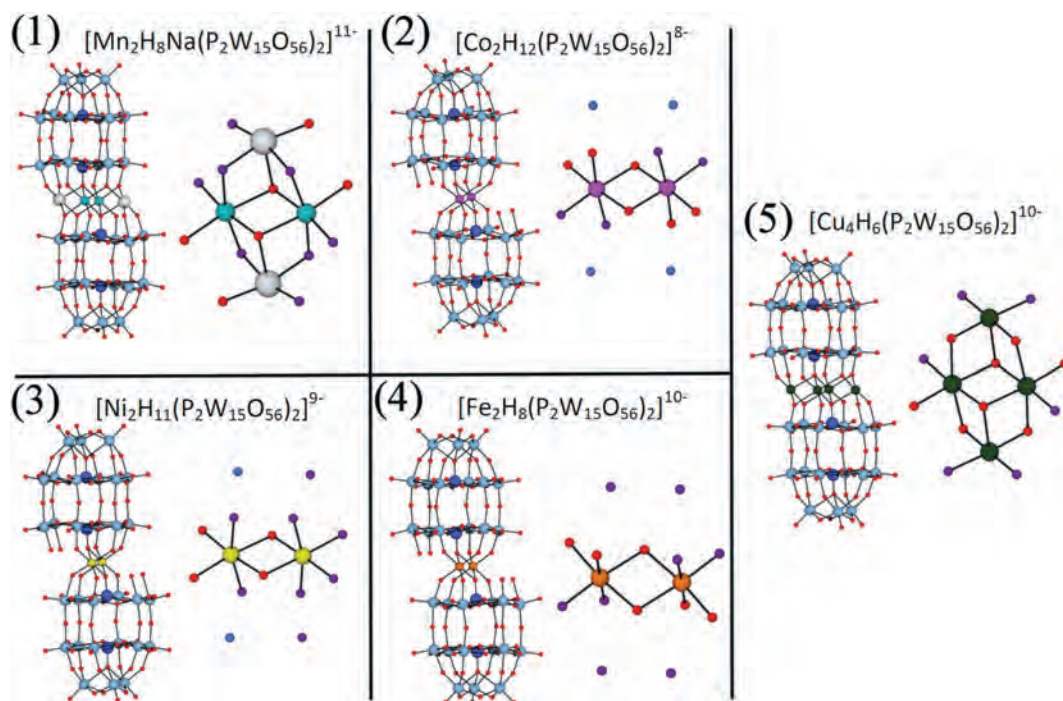


Fig. 2 The structure of clusters 1–5 with the transition metal core highlighted to the right. Structures 1–3 are all dinuclear sandwiches containing M^{II} adopting the $\alpha\beta\beta\alpha$ cluster geometry. Compound 4 contains Fe^{III} and is a different isomer to the first three compounds, the more common $\alpha\alpha\alpha\alpha$ geometry. Compound 5 is a tetranuclear sandwich containing four Cu^{II} ions. In compound 1 one sodium atom is found to be disordered over the two lacunary vacancies in the core, this is shown as a white sphere. In the diagrams of the cluster core the oxygen atoms have been highlighted to show their protonation. Red is unprotonated, purple is singly protonated and blue is deprotonated to give a coordinated water molecule. In the dinuclear cores the four pendant oxygen atoms on the cluster are also shown so that their protonation can be ascertained.

functionalization in low polarity solvent^{37,38} and also for analysis for example in mass spectrometry which requires species which are soluble in acetonitrile.^{39,40} The protons associated with the cluster are mostly located around the core of the cluster, bonded to some of the oxo ligands. The exact location of these protons can be inferred from bond valence sum calculations, by observing bond lengths from crystallographic data, which can tell us if a particular oxygen atom is associated with two, one, or zero protons.

As can be seen from Fig. 2, the structures of the four dinuclear sandwiches are very similar. Compound 1, the manganese sandwich, is the only cluster of the five to show any evidence of sodium ions binding to the lacunary sites in the transition metal core. Crystallographic measurements show one sodium ion to be partially disordered over the two lacunary sites and flame photoelectron spectroscopy and crystallographic measurements support this observation.

Compound 4, the dinuclear iron sandwich, is the only compound of the five to feature the transition metal with an oxidation state of +3. This is unambiguously calculated by bond valence sum measurements on the iron and confirmed by charge balancing arguments with the calculated number of cations by elemental analysis. A consequence of this is that the iron sandwich forms a different isomer to the other sandwich compounds due to the smaller more highly charged ion preferring shorter bonds to the POM cluster. In Fig. 1(c) the two different binding sites are shown. In all of our compounds except for 4 the transition metal ion binds preferentially in the location of the blue

triangles, but in the case of Fe^{III} the red location is preferred and this might be due to the higher charge and smaller size of Fe^{III} centres. A convention for the nomenclature of these isomers was presented by Hill *et al.* in their review of iron sandwich compounds in 2002.³¹ The convention states that the two $\{W_3\}$ caps which are at the ends of the cluster are defined as α and then at the junction where the transition metal core is found if the substituted transition metals are in the same orientation as the cap it is an α junction, and if the orientation is flipped it is a β junction (Fig. 3). By this method we can say that compounds 1, 2, 3, and 5 are $\alpha\beta\beta\alpha$ isomers and the Fe sandwich, compound 4 is an $\alpha\alpha\alpha\alpha$ isomer. As stated earlier, all previously reported dinuclear sandwiches are of the $\alpha\alpha\alpha\alpha$ form so compounds 1–3 are the first reported examples of the $\alpha\beta\beta\alpha$ cluster geometry.

When the reaction which forms these lacunary dinuclear transition metal sandwiches is performed using equimolar copper sulphate as the transition metal salt the full plenary tetranuclear copper(II) sandwich is formed. In the core of this sandwich are found four copper(II) ions, two of which are six coordinate with octahedral bonds to the two clusters. The other two copper ions in the structure are only five-coordinate, displaying square-based pyramidal geometry with a vacant coordination site where a water molecule would tend to be located. This geometry is not uncommon for copper but it is different from the previously reported examples of this compound²⁰ which both feature coordinated water molecules. Attempts to form the dinuclear copper sandwich by this method by lowering the molar ratio of copper in the reaction system were unsuccessful which is interesting

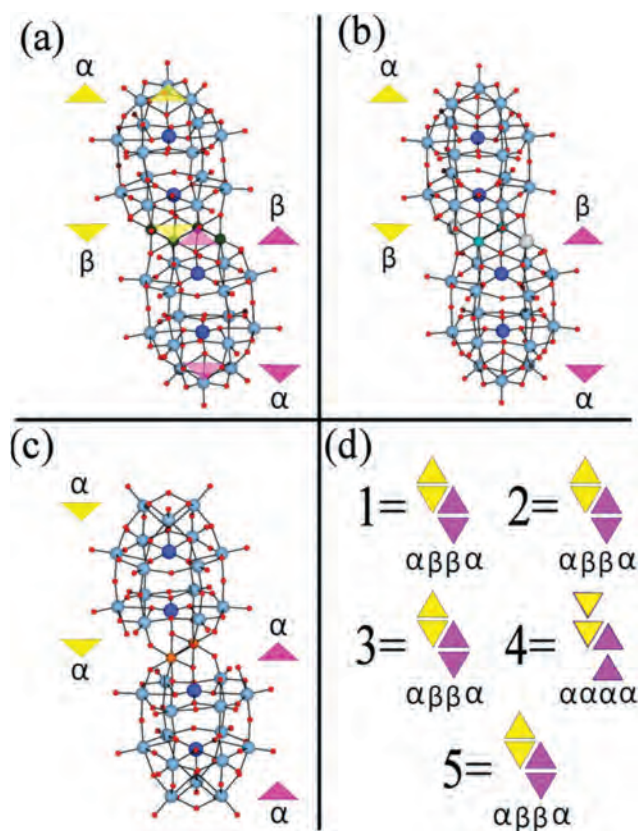


Fig. 3 Showing how the nomenclature for the different isomers is determined. (a) Compound **5**. The isomerism is determined by the orientation of the $\{W_3\}$ cap in the $\{P_2W_{15}\}$ moiety and $\{Cu_3\}$ triangle that completes a conventional Dawson cluster at the joint position. In this example the four Cu centres form two $\{Cu_3\}$ triangles (yellow and pink), each of which is orientated differently with respect to the same-coloured $\{W_3\}$ cap triangle in individual Dawson clusters. Conformation of the structure is labelled $\alpha\beta\beta\alpha$. (b) Compound **1**, **2** and **3**. In these cases, there are lacunary vacancies (Z, grey coloured positions). Each of the two $\{M_2Z\}$ ($M = Mn, Co$ or Ni) triangles is orientated differently with respect to the same-coloured $\{W_3\}$ cap triangle in individual Dawson cluster. Conformation of the structure is labelled $\alpha\beta\beta\alpha$. (c) Compound **4**. In the dinuclear iron sandwich, each of the two $\{Fe_2Z\}$ triangles is orientated similarly with respect to the same-coloured $\{W_3\}$ cap triangle in individual Dawson cluster. Conformation of the structure is labelled $\alpha\alpha\alpha\alpha$, which is isomeric to that of compound **1–3**. Compound **4** adopts this structure because of the higher charged iron(III) ion preferring shorter bonds to the $\{P_2W_{15}\}$ moieties. (d) Showing the isomeric forms of compounds **1–5**.

when considering that copper is one of only a few examples of previously published dinuclear sandwiches.²⁷

Cyclic voltammetry

The redox behaviour of compounds **1–5** were studied in acetonitrile solution. Table 2 shows the main characteristic peaks associated with W redox couples of compounds **1–5** between -2.000 V and $+1.900$ V vs. Ag/Ag^+ at the scan rate region of 100 mV s^{-1} . The form of the diagram remained identical independent of the scanning potential direction. At a scan rate of 100 mV s^{-1} and scanning towards the negative region of

Table 2 Positions of the relative W centred redox peaks for compounds **1–5** as determined by cyclic voltammetry. Values are reported in Volts

	1	2	3	4	5
1st	-0.102	-0.284	-0.175	-0.123	—
2nd	-0.484	-0.438	-0.418	-0.478	—
3rd	-0.751	-0.797	-0.723	-0.796	—
4th	-1.118	-1.155	-1.015	-1.130	—
5th	-1.325	-1.335	-1.251	-1.309	-1.352
6th	-1.660	-1.574	-1.619	-1.530	-1.529
7th	—	-1.736	-1.871	—	-1.681

potential values, 6 (for **1**), 7 (for **2**), 7 (for **3**), 6 (for **4**) and 3 (for **5**) closed spaced quasi-reversible redox waves were observed, respectively. Table 2 summarizes the $E_{1/2}$ values observed for the W-centred redox processes. The cyclic voltammograms of the compounds are represented in figures presented in the ESI.† The peak currents related to the tungsten redox processes were proportional to the square root of the scan rate, (see insets on the ESI† graphs) suggesting that redox processes are diffusion-controlled. In the case of compound **1** it was possible to detect an ill-defined oxidation peak centred at $+0.275$ V which can be assigned to oxidation of Mn(II) centres to Mn(III). On potential reversal the counter redox process takes place before the reduction of the tungsten metal centres which helped us assign unambiguously the remaining waves to W-centred reductions. Compound **2** gave us a similar pattern for the W-redox waves shifted to slightly more negative values. In this case the existence of the Co(II) centres are not electroactive within the negative potential domain being explored here which makes the assignment of the reduction peaks easier. The nickel compound, **3**, continues this trend and once again only the tungsten redox waves are observed. In the case of compound **4** the reduction of Fe(III) metal centres overlaps with the W-redox waves making the assignment of the latter process complicated. Nevertheless, after completing the first cycle it is possible to observe the oxidation of the iron centres back to their initial oxidation state with the two corresponding waves located at $+0.181$ and $+0.321$ V. It is important to note that the two Fe centres are oxidized stepwise in agreement with the previously reported electrochemical studies in aqueous medium of $[Fe_m(X_2W_{15}O_{56})_2]^{n-}$ (where $X = As$ or P and $m = 2, 3$ or 4).^{41–43}

As expected in compound **5**, the characteristic pattern originating from the Cu-centred waves conceal the first four consecutive W-reduction processes. It was possible though to assign the remaining three waves (V, VI and VII) and allow us to draw useful conclusions regarding the influence of the incorporated transition metal on the redox potentials of the tungsten centres.

Comparing the electrochemical behaviour of compounds **1–5** we can observe the similar processes which take place, as was expected. The observed $E_{1/2}$ potential values are in agreement with previously reported W-based POMs, even though important differences in potential locations can be observed depending on the experimental conditions.^{44–49} Overall, the observed patterns associated with the reduction of the tungsten centres are shifted towards more negative values according to the electronegativity

of the transition metals as well as on the overall charge of the clusters.

Conclusions

In conclusion, five new Weakley-type $\{P_2W_{15}\}$ Dawson sandwich compounds have been made by a new synthetic procedure which crystallises the clusters with TBA cations. Four of these are the lacunary dinuclear sandwiches for the transition metals Mn, Fe, Co, and Ni. These are formed with an isomeric geometry, $\alpha\beta\beta\alpha$, as yet unreported for dinuclear sandwiches, which normally form $\alpha\alpha\alpha\alpha$ junctions between the POM and the transition metal core. Compound **4**, the dinuclear iron(III) sandwich, has been reported previously as an As-centred Dawson,²⁶ but its structure is mentioned again here because our reported procedure enables access to the tetrabutylammonium salt as opposed to the sodium salt. Compound **5**, the tetranuclear copper(II) sandwich, also has a similar cluster geometry to a previously reported example except two of the copper atoms are pentacoordinate with missing coordinated water molecules (reported here as a TBA salt). CV measurements of these compounds show that as the transition metal becomes more electronegative, the tungsten redox peaks are shifted to more negative values. This type of sandwich compound has been shown to be effective at catalyzing the reduction of nitrite in a similar way to metalloporphyrins,²⁴ and the clusters reported here could be useful in developing novel organic soluble mixed metal sandwich clusters having potential applications in organo-catalysis and for the development of new magnetic materials.

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