Journal of Inorganic and General Chemistry
ZAAC
Zeitschrift für anorganische und allgemeine Chemie
www.zaac.wiley-vch.de
RESEARCH ARTICLE

DOI: 10.1002/zaac.202200112

An Inorganic Pac-Man: Synthesis, structure and electrochemical studies of a heterometallic {YCo^{II}_3W} cluster sandwiched by two germanotungstates

Masooma Ibrahim,*[a] Israël M. Mbomekallé,[b] Pedro de Oliveira,[b] Thomas Bergfeldt,[c] and Christopher E. Anson[d]

Dedicated to Prof. Dr. Dieter Fenske on his 80th birthday

A new heterometallic sandwich-type Keggin polyoxometalate, $[(GeW_9O_{34})_2\{YCo(W{=}O)(\mu_3\text{-}O)(\mu_3\text{-}OH)(\mu_2\text{-}O)(\mu_2\text{-}OH_2)(OH_2)(C_2H_3O_2)\}]^{13-}$ has been synthesized by a simple reaction method. The isolated compound has been structurally characterized by single crystal X-ray diffraction (SC-XRD), Fourier transform infrared (FTIR) spectroscopy, elemental analysis, and thermogravimetric (TG) analysis. In addition, electrochemical properties have been investigated in detail. The X-ray structure of this POM reveals that a unique heterometallic core $\{YCo_3(W{=}O)(\mu_3\text{-}O)(\mu_3\text{-}OH)(\mu_2\text{-}O)(\mu_2\text{-}OH_2)(OH_2)(OAc)\}^{7+}$ is sandwiched between two $[GeW_9O_{34}]^{10-}$ ligands, giving rise to the first example of a heterometallic core composed of 3d–4d–5d transition metal ions.

Introduction

Polyoxometalates (POMs) are polynuclear metal-oxo complexes of early transition metals (e.g. M = V^V, Mo^{VI}, W^{VI}, Ta^V, Nb^V) that are bridged by oxo ligands (O^{2-}) to form closed 3-dimensional frameworks. They hold substantial structural and compositional versatility, allowing the tuning of their electronic structure and consequently their functionality.[1] They have demonstrated great potential in a wide range of fields, such as catalysis,[2] energy,[3,4] medicine,[5,6] imaging,[7] magnetism,[8,9] and materials science.[10] Particularly, metal-substituted POMs (MSPs) have become one of the most investigated subclasses of POMs by virtue of their structural diversity, rich redox properties and significant applications. Lacunary POMs as multidentate O-donor ligands have a good affinity for various electrophiles, such as transition metal (TM)[11] or rare earth (RE) centers[12] to generate diverse structures with interesting properties. Among the multitude of RE-containing POMs, Y^{III} embedded POMs are very limited.[13–18]

Recently, increasing interest and efforts have been devoted to the synthesis of 3d–4f heterometallic substituted POMs as one of the promising approaches to tune up the chemical and physical properties of the materials at the atomic level. However, it is still challenging to synthesize heterometallic clusters within the POM skeleton, since the oxophilic 4f cations usually possess high reactivity with highly negative polyanions, which often results in precipitation rather than crystallization. Furthermore, the difference in radius/coordination number of the 3d and the 4f centers induces competitive reactions between them which leads to the isolation of only one type of metal ion containing POMs, while the second metal type remains as a mere surface decoration or linker. So far, one-pot synthetic procedures have only succeeded in only a few examples of POM-based 3d–4f heterometallic aggregates.[19–24] The transition metal yttrium is also a rare earth element, as its chemistry and physical properties are extremely comparable to the lanthanides. Therefore, similar to 3d–4f heterometallic POMs, the exploration of 3d–Y heterometallic clusters with POM ligands also remains an ongoing challenge and the number of such materials is very small.[22,25–28]

Herein, we report the synthesis of $Na_{10}(H_3O)_3[(GeW_9O_{34})_2\{YCo(W{=}O)(\mu_3\text{-}O)(\mu_3\text{-}OH)(\mu_2\text{-}O)(\mu_2\text{-}OH_2)(OH_2)(C_2H_3O_2)\}]\cdot 60H_2O$ (**Na-1**), its structural characterization in the solid state and its electrochemical behavior in aqueous solutions.

[a] *M. Ibrahim*
Institute of Nanotechnology (INT), Karlsruhe Institute of Technology, Hermann von-Helmholtz Platz 1, 76344 Eggenstein-Leopoldshafen, Germany
E-mail: masooma.ibrahim@kit.edu
[b] *I. M. Mbomekallé, P. de Oliveira*
Equipe d'Electrochimie et de Photo-électrochimie, Institut de Chimie Physique, Université Paris-Saclay, UMR 8000 CNRS, Orsay F-91405, France
[c] *T. Bergfeldt*
Institute for Applied Materials (IAM-AWP), Karlsruhe Institute of Technology (KIT), Postfach 3640, 76021 Karlsruhe, Germany
[d] *C. E. Anson*
Institute of Inorganic Chemistry, Karlsruhe Institute of Technology, Engesserstrasse 15, 76131 Karlsruhe, Germany

Supporting information for this article is available on the WWW under https://doi.org/10.1002/zaac.202200112

© 2022 The Authors. Zeitschrift für anorganische und allgemeine Chemie published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution Non-Commercial License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.

© 2022 The Authors. Zeitschrift für anorganische und allgemeine Chemie published by Wiley-VCH GmbH

Results and Discussion

Synthesis and Structure

The heterometallic cluster containing sandwich-type tungstogermanate: $[(GeW_9O_{34})_2\{YCo(W{=}O)(\mu_3\text{-}O)(\mu_3\text{-}OH)(\mu_2\text{-}O)(\mu_2\text{-}OH_2)(OH_2)(C_2H_3O_2)\}]^{13-}$ (**1**) has been synthesized under mild bench reaction conditions by reacting $YCl_3\cdot 6H_2O$, $CoCl_2\cdot 6H_2O$ and the trilacunary POM ligand $Na_{10}[A\text{-}\alpha\text{-}GeW_9O_{34}]\cdot 18H_2O$ in lithium acetate buffer solution of pH 6.6. The resultant product **Na-1** was characterized in the solid state by single crystal XRD, FTIR, TGA and elemental analysis.

The X-ray structure of **Na-1** shows that it crystallizes in the monoclinic crystal system with space group *C2/m*. Polyanion **1** comprises an unprecedented, sandwich-type structure with a central heterometallic core $\{YM_4\}$ embedded between two $\{GeW_9O_{34}\}$ POM ligands (Figure 1). In the central pentanuclear square-pyramidal $\{YM_4\}$ unit, one M is W(VI), equally disordered over the four M sites, the other three M are Co(II). A consequence of this metal disorder is a disorder of the ligands coordinated to the YCo_3W square-pyramid. Any oxygen atom bonded to the W atom in this moiety will be fully-deprotonated. Thus, whichever of the O(26) or the O(28) bridges between Y(1) and two Co will be (μ_3-OH), while the other, bridging between Y(1), a Co and the W will be (μ_3-O). Similarly, whichever of the O(27) or the O(27′) bridges between two Co atoms will be (μ_2-OH_2), as is usual for divalent metals, while the other, bridging between Co and W, will be (μ_2-O). For the terminal oxygen sites on these four metals, that bonded to the W will clearly be (W=O), while that on the symmetry-equivalent Co will be a water. The other pair of symmetry-equivalent metals, both being Co centres, are then bridged by a syn,syn-acetate ligand (Figure 2).The YCo_3W moiety can thus be formulated as $\{YCo^{II}_3(W{=}O)(\mu_3\text{-}O)(\mu_3\text{-}OH)(\mu_2\text{-}O)(\mu_2\text{-}OH_2)(OH_2)(\mu_2\text{-}\mu^1,\mu^1\text{-}OAc)\}^{7+}$. The overall charge of the polyanion is 13^-, which is balanced by 10 sodium cations and three hydronium ions $(H_3O)^+$. These findings are complemented by elemental analyses. Bond valence sum (BVS) gives 6.0–6.1 for the non-disordered W. Whereas, for the disordered W/Co BVS is not a reliable option to determine the valence sates in a quantitative way. Apparently, the pink color of the crystals is also an indication of Co(II) and the absence of a deep blue to bronze color should mean that W mixed-valency can be excluded and so rule out any reduction to W(V). The Y^{III} ion in the heterometallic core has a square antiprismatic geometry, its coordination sites are fulfilled by six oxygen atoms from two $[GeW_9O_{34}]^{10-}$ trilacunary ligands, one μ_3-OH and one μ_3-O ligands. The Co^{II} ions incorporated in the cavity of the POM ligands are hexa-coordinated, possessing an octahedral geometry. This complex is the first example of a heterometallic POM that contains a central core made up of three types of transition metals (3d–4d–5d).

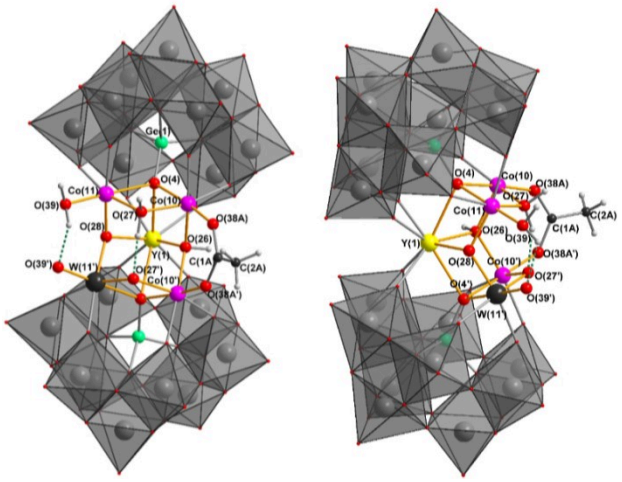


Figure 1. Two views of the heterometallic POM in **Na-1**, showing one of the four possible positions of the W ion within the square Co_3W face of the central $\{YCo_3W\}$ moiety with the corresponding arrangement of ligands. The trilacunary $(GeW_9O_{34})^{10-}$ POM metallaligands are shown in polyhedral representation, and intramolecular hydrogen bonds as green dashed lines.

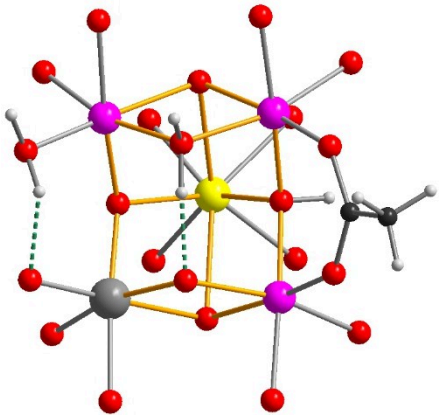


Figure 2. The heterometallic moiety $\{YCo_3W\}$ in **1**. Color scheme for balls: Y = yellow, Co = pink, W = dark grey, O = red, C = black, and H = light grey. Intramolecular hydrogen bonds as green dashed lines.

Fourier Transform Infrared Spectroscopy

The IR spectra of **Na-1** and the trilacunary ligand $Na_{10}[A\text{-}\alpha\text{-}GeW_9O_{34}]\cdot 18H_2O$ have been recorded between 2000 and 400 cm^{-1} (Figure S1, Supporting Information). They display the characteristic vibration patterns derived from the Keggin framework in the low-wavenumber region. The difference/shift in the characteristic bands of the IR spectra of the lacunary precursor and the synthesized compound indicate the formation of a new species. The characteristic vibration bands attributed to the metal-oxygen bonds observed in **Na-1** are listed in the Experimental Section.

Thermogravimetric Analysis

The thermal stability of compound **Na-1** has been investigated in flowing N_2 atmosphere with heating rate of 10 °C min^{-1} in

© 2022 The Authors. Zeitschrift für anorganische und allgemeine Chemie published by Wiley-VCH GmbH

the temperature range 25–1000 °C. Thermogravimetric analysis (TGA) of the POM showed one successive weight loss step in the temperature range 25–925 °C (Figure S2, Supporting Information). The total weight loss is ca. 13 %, corresponding to the removal of 41 crystal water molecules and coordinated water molecules, hydroxo ligand and acetate group (at higher temperatures). This result is slightly lower to the 60 water molecules determined by elemental analysis. The discrepancy may be due to different drying conditions of the bulk samples.

Electrochemical Characterization

The electrochemistry of **Na-1** has been investigated by cyclic voltammetry (CV). Figure 3A shows the CVs of **Na-1** (black) and of the $[GeW_9O_{34}]^{10-}$ lacunary POM (red), the concentrations having been adjusted to facilitate comparison. The redox behaviours of the two compounds, although very similar, differ in some respects. The reduction process of the **Na-1** tungstic centres is slower than that of the $\{GeW_9\}$ tungstic centres, yet the reduction peak potential value is the same for both compounds: −0.82 V vs. SCE. During the reverse scan, the re-oxidation occurs in two distinct steps and the oxidation peak potentials are different for the two compounds (see Table 1). If the potential window is restricted between 0.6 V and −1.1 V vs. SCE, there is no change in the surface of the working electrode and the electron transfer process remains controlled by diffusion (Figure S3A). When the potential window is extended to 1.5 V vs. SCE, the oxidation wave attributable to the Co(II) centres appears between 1.25 and 1.35 V vs. SCE (Figures 3B and S3B). As is often the case with the cobalt-containing POMs, the Co(II) oxidation wave is not very visible,[29] but there is a modification of the working electrode surface which results in a shift of the reduction wave towards the negative potentials during the second scan cycle (from −0.82 V to −0.91 V vs. SCE).

When moving to higher pH values, there is a shift of the whole CV towards the negative potential side. This results in a greater difficulty in reducing the tungstic centres, with a consequent potential shift of $\Delta E = 220$ mV (Figure 4A and Table 1). On the oxidising potential side, the oxidation wave of the Co(II) centres appears at lower potentials ($E \approx 0.9$ V vs. SCE), but above all it is followed by a catalytic wave attributed to the oxidation of water, a property widely observed with cobalt-containing POMs (Figure 4B).[30,31] However, the compound is only stable enough in solution for 6 hours so that its electrochemical behavior could be characterized. Since the catalytic studies require longer times (at least 24h) and the compound turned out to decay after 8h in solution, we were not able to carry them out.

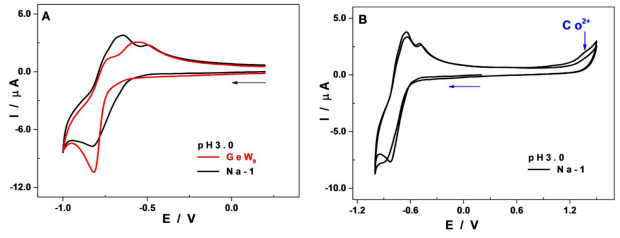


Figure 3. (A) CVs of **Na-1** (black) and **GeW_9** (red) with the potential window restricted between 0.6 V and −1.1 V. (B) CVs of **Na-1**, two successive cycles recorded with the potential window extended up to 1.5 V. The CVs are recorded at a scan rate of 20 $mV.s^{-1}$ in 0.5 M $Li_2SO_4 + H_2SO_4$/pH 3.0. POM concentrations: [**Na-1**] = 0.33 mM, $(GeW_9O_{34})^{10-}$ = 0.76 mM. Working electrode: GC; counter electrode: Pt gauze; reference electrode: SCE.

Table 1. Reduction, Ec, and oxidation, Ea, peak potentials (mV vs SCE) measured from the CVs of **Na-1** and of $(GeW_9O_{34})^{10-}$ recorded in the experimental conditions specified above.

		W Ec	W Ea_1	W Ea_2	Co Ea
pH 3	**GeW_9**	−0.82	−0.56	−0.73	
	Na-1	−0.82	−0.64	−0.74	> 1.25
pH 5	**Na-1**	−1.04	−0.80	−0.97	> 0.90

Conclusions

In summary, we have synthesized an unusual heterometallic POM $Na_{10}(H_3O)_3[(GeW_9O_{34})_2\{YCo(W{=}O)(\mu_3\text{-}O)(\mu_3\text{-}OH)(\mu_2\text{-}O)(\mu_2\text{-}OH_2)(OH_2)(C_2H_3O_2)\}] \cdot 60H_2O$ (**Na-1**) under mild reaction conditions and structurally characterized it by a variety of analytical techniques such as X-ray crystallography, IR spectroscopy, elemental analysis and TGA. In addition, the electrochemical properties of **1** have also been evaluated in aqueous media. To the best of our knowledge, **Na-1** represents the first example of a 3d–4d–5d heterometallic cluster $\{YCo^{II}_3W\}$ containing sandwich-type POM. The successful synthesis of this heterometallic POM will opens the way for further exploring the heterometallic POM chemistry. The extension of this family of POMs to other 3d and 4f centers is currently in progress. We aim to explore variations to the metal ions within $\{YCo_3W\}$ core in order to tune their electronic properties. Particularly, in case of paramagnetic 4f containing $\{LnCo_3W\}$-POMs, $\{YCo_3W\}$-POMs will be helpful in deleting magnetic contributions to the overall picture

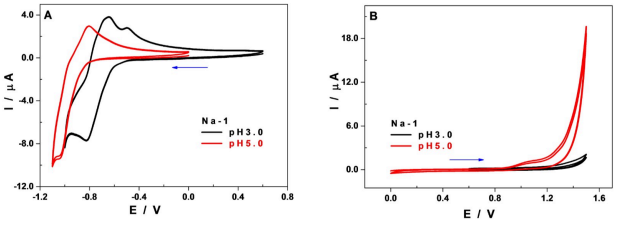


Figure 4. CVs of **Na-1** in 0.5 M $Li_2SO_4 + H_2SO_4$/pH 3.0 (black) and in 1.0 M $LiCH_3CO_2 + CH_3CO_2H$/pH 5.0 (red). (A) Potential window restricted between 0.6 V and −1.15 V. (B) Potential window restricted between 0.0 V and 1.5 V. The CVs are recorded at a scan rate of 20 $mV.s^{-1}$. POM concentration: [**Na-1**] = 0.33 mM. Working electrode: GC; counter electrode: Pt gauze; reference electrode: SCE.

© 2022 The Authors. Zeitschrift für anorganische und allgemeine Chemie published by Wiley-VCH GmbH

of paramagnetic lanthanide (Ln^{III}) {$LnCo_3W$} analogue through diamagnetic Y^{III} cation.

Experimental Section

Synthesis of $Na_{10}(H_3O)_3[(GeW_9O_{34})_2\{YCo(W{=}O)(\mu_3\text{-}O)(\mu_3\text{-}OH)(\mu_2\text{-}O)(\mu_2\text{-}OH_2)(OH_2)(C_2H_3O_2)\}].60H_2O$ (**Na-1**)

$CoCl_2\cdot 6H_2O$ (1.07 g, 4.5 mmol) was dissolved in 100 mL of 1 M lithium acetate buffer of pH 6.6. Then, $Na_{10}[A\text{-}\alpha\text{-}GeW_9O_{34}]\cdot 18H_2O$ (5.33 g, 2.0 mmol) was added to this solution with stirring. Afterwards 3.0 mL of 1 M $YCl_3\cdot 6H_2O$ (0.9 g, 3.0 mmol) were added to the clear pink solution. The resultant turbid solution was stirred and heated at 90 °C for one hour. Subsequently on cooling, the precipitate formed was filtered off. Slow evaporation of the solvent at room temperature for about three weeks led to the formation of pink crystals suitable for X-ray diffraction. The crystalline product was isolated using filtration and washed successively with cold water, in order to remove the traces of adsorbed acetate buffer solvent from the material before using it for bulk analysis and electrochemical studies. The bulk purity of the product was established using elemental analysis. In addition, the purity of the product was also determined by FTIR using the separated crystals of **Na-1** as reference. The perfect match of the two spectra obtained from the IR studies of separated crystals and bulk materials provide convincing evidence for purity of the bulk product (Figure S1).

Yield: 0.80 g (12% based on W). IR νmax (cm^{-1}; KBr pellets): 988 (w; ν_{as}(W–O_d)), 968 (w; ν_{as} (W–O_b–W)), 844 (s; ν_{as}(Ge–O)), 849 (w; ν_{as} (W–O_c–W)), 651 and 619 (s; δ(O–Ge–O)/δ(W–O–W)), 561, 523 and 438 (m; δ(O–Ge–O)/δ(W–O–W)/δ(W–O–Ge)/δ(W–O–Y)/δ(W–O–Co)). Elemental analysis for **Na-1**, calculated (found) % : Na 3.54 (3.52), Ge 2.23 (2.22), Co 2.72 (2.84), Y 1.37 (1.42), W 53.72 (53.90) %.

Crystallographic Experimental

A pink block-shaped crystal was coated in Fomblin oil and mounted on a Stoe Stadi-Vari diffractometer equipped with a MetalJet-2 liquid-Ga rotating anode source. Data were corrected for polarisation and absorption effects. The strucutre was solved using direct methods (intrinsic-phasing: SHELXT[32]) and refined by full-matrix least-squares refinement against all data (SHELXL-2018[33]). Ordered atoms were assigned anisotropic thermal parameters, as were the disordered metal sites Co(10)/W(10) and Co(11)/W(11).

Refinement of the metal sites Co(10) and Co(11) and their symmetry-equivalents as Co resulted in temperature factors significantly lower than for the other metal atoms in the structure. Refinement of these sites as mixed Co/W converged with occupancies close to 75% Co and 25% W and their temperature factors in line with those of the other metals; their Co and W occupancies were then fixed at 0.75 and 0.25, respectively, in all subsequent refinements. This results in a central square-pyramidal YM_4 moiety with the Y in the axial position, and three Co and one W disordered over the four basal sites. This overall formulation as a $Ge_2W_{19}YCo_3$ cluster is in excellent agreement with the metals analysis.

As a result of this disorder, no attempt was made to model the H-atoms in {YM_4} moiety. Although some of the Na^+ counter cations and their water ligands are ordered, several are not, and again no attempt was made to model their H-atoms.

Details of the data collection and structure refinement are summarised in Table 2. Full crystallographic data for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 2157252. Copies of the data can be obtained, free of charge, from https://www.ccdc.cam.ac.uk/structures/

Table 2. Crystal Data.

Compound	**Na-1**
Formula	$C_2H_{137}Co_3Ge_2Na_{10}O_{139}W_{19}Y$
Formula weight	6520.04
Crystal System	Monoclinic
Space Group	*C2/m*
a/Å	13.1860(2)
b/Å	37.8503(6)
c/Å	22.4343(3)
β/°	99.722(1)
V/Å^3	11036.0(3)
Z	4
T/K	180(2)
F(000)	11844
D_c/Mg m^{-3}	3.924
μ(Ga–Kα)/mm^{-1}	29.603
Data Measured	39068
Unique Data	12478
R_{int}	0.0784
Data with $I \geq 2\sigma(I)$	12142
wR_2 (all data)	0.1673
S (all data)	1.158
R_1 [$I \geq 2\sigma(I)$]	0.0609
Parameters/Restraints	727/3
Largest diff. peak/hole/eÅ^{-3}	+2.22/−3.81
CCDC number	2157252

Electrochemical Characterization

Pure water was obtained with a Milli-Q Integral 5 purification set. All reagents were of high-purity grade and were used as purchased without further purification: CH_3CO_2H (Glacial, Prolabo Normapur), H_2SO_4 (Sigma Aldrich), $Li_2SO_4.H_2O$ (Acros Organics) and $LiCH_3CO_2.2H_2O$ (Acros Organics). The composition of the various media was as follows: for pH 3.0, 0.5 M $Li_2SO_4 + H_2SO_4$ and for pH 5.0, 1.0 M $LiCH_3CO_2 + CH_3CO_2H$. The stability of the compound in solution was assessed by cyclic voltammetry.

Electrochemical data were obtained using an EG & G 273 A potentiostat driven by a PC with the M270 software. A divided cell with a standard three-electrode configuration was used for cyclic voltammetry experiments. The reference electrode was a saturated calomel electrode (SCE) and the counter electrode a platinum gauze of large surface area; both electrodes were separated from the bulk electrolyte solution via fritted compartments filled with the same electrolyte. The working electrode was a 3 mm outer diameter glassy carbon (GC) from Mersen, France. The pre-treatment of the electrode before each experiment is adapted from a method described elsewhere.[34] Prior to each experiment, solutions were thoroughly de-aerated for at least 30 min with pure argon. A positive pressure of this gas was maintained during subsequent work. All cyclic voltammograms (CVs) were recorded at a scan rate of 20 mV s^{-1} and potentials are quoted against SCE unless otherwise stated. The polyanion concentrations were 0.16 mM for **Na-1** and adjusted for $[GeW_9O_{34}]^{10-}$. All experiments were performed at room temperature, which is controlled and fixed for the laboratory at 20 °C. Results were very reproducible from one experiment to the other and slight variations observed over successive runs are rather attributed to the uncertainty associated with the detection limit of

© 2022 The Authors. Zeitschrift für anorganische und allgemeine Chemie published by Wiley-VCH GmbH

our equipment (potentiostat, hardware and software) and not to the working electrode pre-treatment nor to possible fluctuations in temperature.

Acknowledgements

M.I. thanks Prof. Annie K. Powell for continuous support and guidance. M.I. acknowledges funding by the Helmholtz Gemeinschaft through the program Science and Technology of Nanosystems (STN) and program oriented funding phase four (PoF IV). I.M.M. and P.d.O. thank the CNRS and the Université Paris-Saclay for financial support. We also thank Olaf Fuhr for performing the single crystal X-ray crystallography (SCXRC) measurement. This work was partially carried out with the support from the Karlsruhe Nano Micro Facility (KNMF), a Helmholtz research infrastructure at the Karlsruhe Institute of Technology. COST Action MOLSPIN (CA15128). Open Access funding enabled and organized by Projekt DEAL.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Conflict of Interest

The authors declare no conflict of interest.

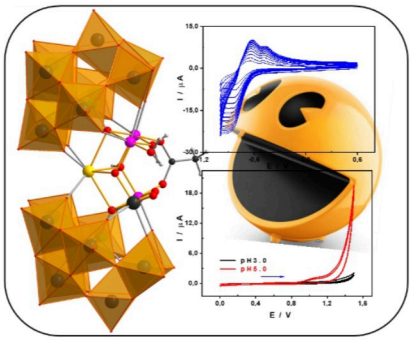
Keywords: heterometallic · polyoxometalates · yttrium · cobalt · electrochemistry

[1] M. I. S. Veríssimo, D. V. Evtuguin, M. T. S. R. Gomes, *Front. Chem.* **2022**, *10*, 1–32.
[2] D. Gao, I. Trentin, L. Schwiedrzik, L. González, C. Streb, *Molecules* **2020**, *25*, 1–20.
[3] M. R. Horn, A. Singh, S. Alomari, S. Goberna-Ferrón, R. Benages-Vilau, N. Chodankar, N. Motta, K. Ostrikov, J. Macleod, P. Sonar, P. Gomez-Romero, D. Dubal, *Energy Environ. Sci.* **2021**, *14*, 1652–1700.
[4] L. Chen, W. L. Chen, X. L. Wang, Y. G. Li, Z. M. Su, E. B. Wang, *Chem. Soc. Rev.* **2019**, *48*, 260–284.
[5] A. Bijelic, M. Aureliano, A. Rompel, *Angew. Chem. Int. Ed.* **2019**, *58*, 2980–2999; *Angew. Chem.* **2019**, *131*, 3008–3029.
[6] A. Bijelic, M. Aureliano, A. Rompel, *Chem. Commun.* **2018**, *54*, 1153–1169.
[7] M. Ibrahim, S. Krämer, N. Schork, G. Guthausen, *Dalton Trans.* **2019**, *48*, 15597–15604.
[8] C. Boskovic, *Acc. Chem. Res.* **2017**, *50*, 2205–2214.
[9] J. M. Clemente-Juan, E. Coronado, A. Gaita-Ariño, *Chem. Soc. Rev.* **2012**, *41*, 7464–7478.
[10] A. V. Anyushin, A. Kondinski, T. N. Parac-Vogt, *Chem. Soc. Rev.* **2020**, *49*, 382–432.
[11] S. T. Zheng, G. Y. Yang, *Chem. Soc. Rev.* **2012**, *41*, 7623–7646.
[12] X. Ma, W. Yang, L. Chen, J. Zhao, *CrystEngComm* **2015**, *17*, 8175–8197.
[13] M. Ibrahim, B. Bassil, U. Kortz, *Inorganics* **2015**, *3*, 267–278.
[14] H. Lou Li, Y. J. Liu, J. L. Liu, L. J. Chen, J. W. Zhao, G. Y. Yang, *Chem. Eur. J.* **2017**, *23*, 2673–2689.
[15] M. Ibrahim, S. S. Mal, B. S. Bassil, A. Banerjee, U. Kortz, *Inorg. Chem.* **2011**, *50*, 956–960.
[16] J. Liu, D. Wang, X. Xu, H. Li, J. Zhao, L. Chen, *Inorg. Chem.* **2021**, *60*, 2533–2541.
[17] K. Suzuki, M. Sugawa, Y. Kikukawa, K. Kamata, K. Yamaguchi, N. Mizuno, *Inorg. Chem.* **2012**.
[18] M. Barsukova, M. H. Dickman, E. Visser, S. S. Mal, U. Kortz, *ZAAC.* **2008**, *634*, 2423–2427.
[19] J. Liu, Q. Han, L. Chen, J. Zhao, *CrystEngComm* **2016**, *18*, 842–862.
[20] J. W. Zhao, Y. Z. Li, L. J. Chen, G. Y. Yang, *Chem. Commun.* **2016**, *52*, 4418–4445.
[21] M. Ibrahim, V. Mereacre, N. Leblanc, W. Wernsdorfer, C. E. Anson, A. K. Powell, *Angew. Chem. Int. Ed.* **2015**, *54*, 15574–15578; *Angew. Chem.* **2015**, *127*, 15795–15799.
[22] M. Ibrahim, Y. Peng, E. Moreno-Pineda, C. E. Anson, J. Schnack, A. K. Powell, *Small Structures* **2021**, *2*, 2100052.
[23] S. Reinoso, *Dalton Trans.* **2011**, *40*, 6610–6615.
[24] S. Reinoso, J. R. Galán-Mascarós, L. Lezama, *Inorg. Chem.* **2011**, *50*, 9587–9593.
[25] L. Chen, J. Cao, X. Li, X. Ma, J. Luo, J. Zhao, *CrystEngComm* **2015**, *17*, 5002–5013.
[26] G. Xue, B. Liu, H. Hu, J. Yang, J. Wang, F. Fu, *J. Mol. Struct.* **2004**, *690*, 95–103.
[27] J. Zhao, D. Shi, L. Chen, P. Ma, J. Wang, J. Zhang, J. Niu, *Cryst. Growth Des.* **2013**, *13*, 4368–4377.
[28] V. Das, R. Gupta, N. Iseki, M. Sadakane, A. S. Mougharbel, U. Kortz, F. Hussain, *ChemistrySelect* **2019**, *4*, 2538–2544.
[29] C. S. Ayingone Mezui, P. De Oliveira, A. L. Teillout, J. Marrot, P. Berthet, M. Lebrini, I. M. Mbomekallé, *Inorg. Chem.* **2017**, *56*, 1999–2012.
[30] G. Zhu, Y. V. Geletii, P. Kögerler, H. Schilder, J. Song, S. Lense, C. Zhao, K. I. Hardcastle, D. G. Musaev, C. L. Hill, *Dalton Trans.* **2012**, *41*, 2084–2090.
[31] X. B. Han, Z. M. Zhang, T. Zhang, Y. G. Li, W. Lin, W. You, Z. M. Su, E. B. Wang, *J. Am. Chem. Soc.* **2014**, *136*, 5359–5366.
[32] G. M. Sheldrick, *Acta Crystallogr.* **2015**, *A71*, 3–8.
[33] G. M. Sheldrick, *Acta Crystallogr.* **2015**, *A71*, 3–8.
[34] N. Vila, P. A. Aparicio, F. Sécheresse, J. M. Poblet, X. López, *Inorg. Chem.* **2012**, *51*, 6129–6138.

Manuscript received: March 19, 2022
Revised manuscript received: July 11, 2022
Accepted manuscript online: July 19, 2022

© 2022 The Authors. Zeitschrift für anorganische und allgemeine Chemie published by Wiley-VCH GmbH

RESEARCH ARTICLE



M. Ibrahim, I. M. Mbomekallé, P. de Oliveira, T. Bergfeldt, C. E. Anson*

1 – 6

An Inorganic Pac-Man: Synthesis, structure and electrochemical studies of a heterometallic $\{YCo^{II}_3W\}$ cluster sandwiched by two germanotungstates