

Systematic approach to the synthesis of cobalt-containing polyoxometalates for their application as energy storage materials

Ángela Barros ^{1*}, Beñat Artetxe ², Unai Eletxigerra ¹, Estibaliz Aranzabe ¹ and Juan M. Gutiérrez-Zorrilla ²

¹ Surface Chemistry and Nanotechnologies Unit, Tekniker, Iñaki Goenaga 5, 20600 Eibar, Spain; unai.eletxigerra@tekniker.es (U.E.); estibaliz.aranzabe@tekniker.es (E.A.)

² Departamento de Química Orgánica e Inorgánica, Facultad de ciencia y Tecnología, Universidad del País Vasco UPV/EHU,, 48080 Bilbao, Spain; benat.artetxe@ehu.eus (B.A.), juanma.zorrilla@ehu.eus (J.M.G.-Z.)

* Correspondence: Correspondence: angela.barros@tekniker.es

Table of contents

Figure S1. FT-IR spectrum and assignation of the most significant bands [33] for the $K_6[Co(H_2O)_4]_2(H_2W_{12}O_{42}) \cdot nH_2O$ side product (ν , stretching mode and δ , bending modes).	1
Table S1. Fitting parameters for the PXRD pattern of K-Co₂W₁₁	1
Figure S3. UV-Vis absorption spectra for the reaction mixture at $t = 0$ min and $t = 20$ min, in comparison to the freshly prepared solution of K-Co₂W₁₁ dissolved in deionised H ₂ O.	2
Figure S4. UV-Vis absorption spectra for K-Co₂W₁₁ and K-CoW₁₂ in deionised H ₂ O.	2
Figure S5. TGA curve of K-CoW₁₂	3
Figure S6. FT-IR spectrum of K-CoW₁₂ obtained after acidification of K-Co₂W₁₁ in 2M H ₂ SO ₄ with the corresponding assignation of the bands for CoW₁₂ and SO ₄ ²⁻ species, respectively [30], [44]. ..	3
Table S2. Yields of the reactions carried out at different pH conditions to evaluate the transition from Co₂W₁₁ to CoW₁₂	3
Figure S7. FT-IR spectra of the solid products isolated from the acidification of a solution of K-CoW₁₂ with aqueous 1M HCl or H/LiAc. The assignment revealed that the solid isolated from the reaction with HCl corresponds to K-CoW₁₂ (small letters), whereas that from H/LiAc agrees with K-Co₂W₁₁ (capital letter). Find the detailed band assignation for K-Co₂W₁₁ and K-CoW₁₂ in the manuscript enclosed in Figures 2 and 3, respectively.	4
Figure S8. UV-Vis absorption spectra (left) for different concentrations (20-120 mM) in 1M H/LiAc buffer of K-CoSiW₁₁ prepared following previously reported procedures, together with its calibration curve (right).	4
References	4

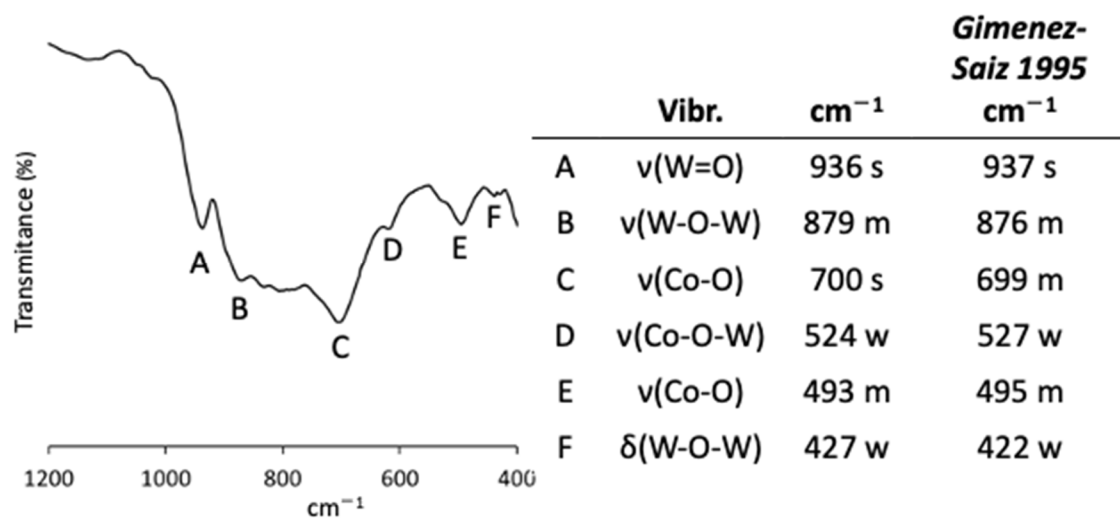


Figure S1. FT-IR spectrum and assignation of the most significant bands [33] for the $K_6[\{Co(H_2O)_4\}_2(H_2W_{12}O_{42})] \cdot nH_2O$ side product (v, stretching mode and δ , bending modes).

Table S1. Fitting parameters for the PXRD pattern of $K-Co_2W_{11}$.

Lattice parameters	Agreement factors
Cubic, $Pm-3m$	$R_{Bragg} = 2.59$
$a = 10.71(2) \text{ \AA}$	$\chi^2 = 2.16$

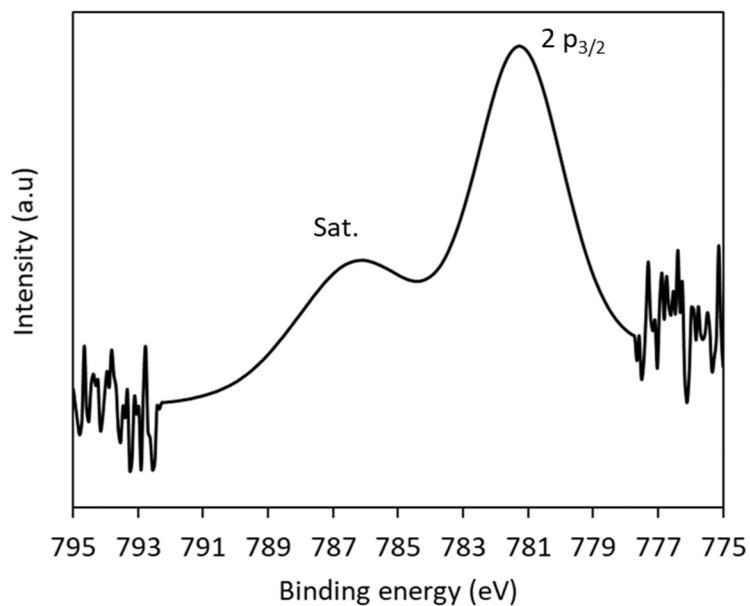


Figure S2. XPS spectrum of Co 2p peak for $K-Co_2W_{11}$.

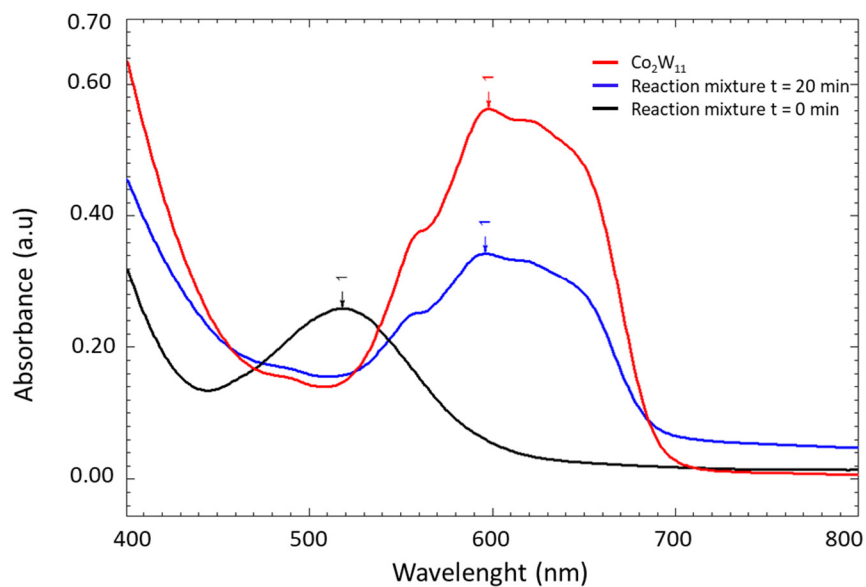


Figure S3. UV-Vis absorption spectra for the reaction mixture at $t = 0$ min and $t = 20$ min, in comparison to the freshly prepared solution of $\text{K-Co}_2\text{W}_{11}$ dissolved in deionised H_2O .

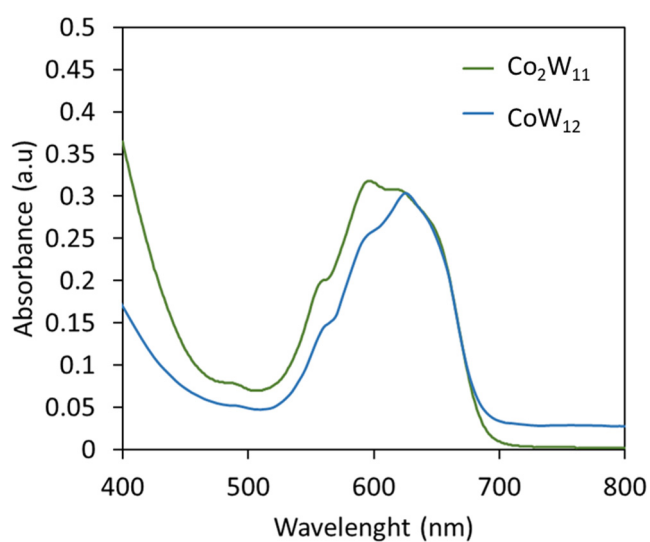


Figure S4. UV-Vis absorption spectra for $\text{K-Co}_2\text{W}_{11}$ and K-CoW_{12} in deionised H_2O .

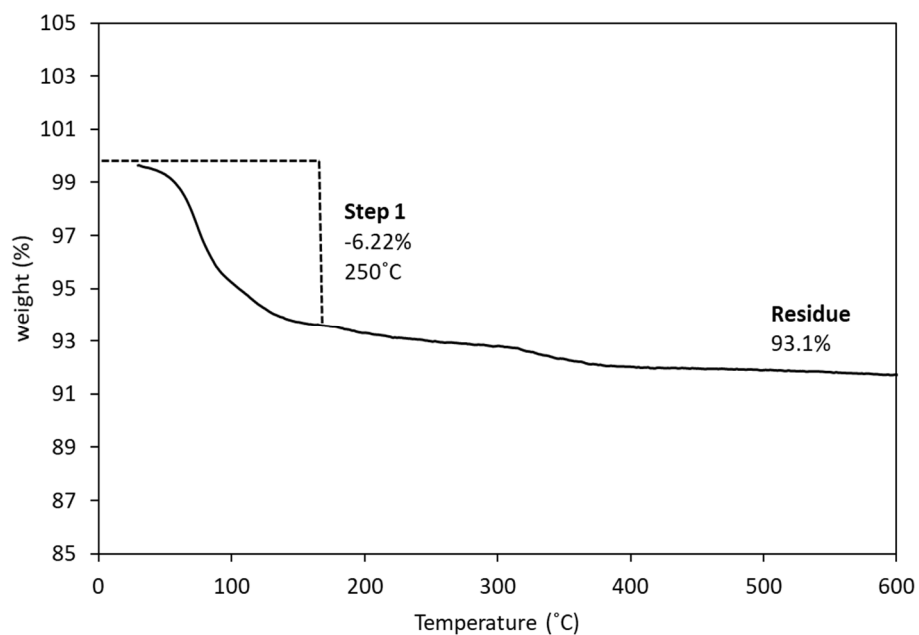


Figure S5. TGA curve of K-CoW₁₂.

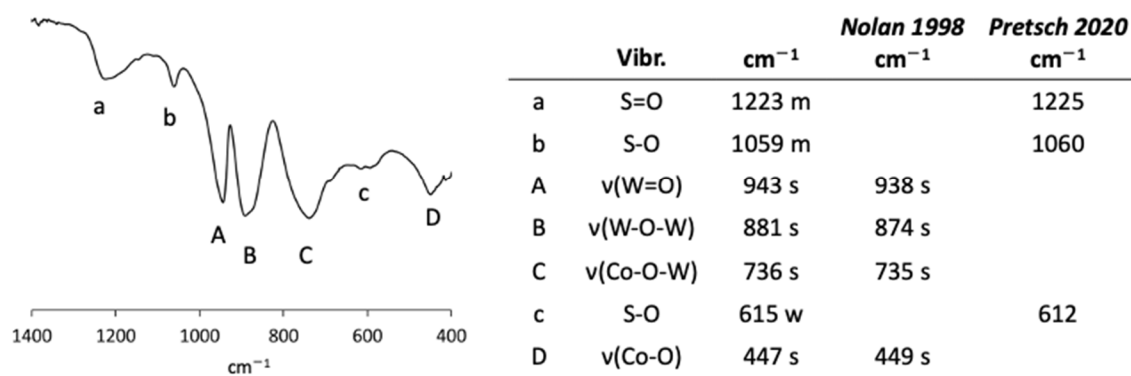


Figure S6. FT-IR spectrum of K-CoW₁₂ obtained after acidification of K-Co₂W₁₁ in 2M H₂SO₄ with the corresponding assignment of the bands for CoW₁₂ and SO₄²⁻ species, respectively [30], [44].

Table S2. Yields of the reactions carried out at different pH conditions to evaluate the transition from Co₂W₁₁ to CoW₁₂.

Acid	pH	Yield (%)
1M HCl	0	88±10
1M H ₂ SO ₄	0	22±7
1M HCOOH (HForm)	2	-
1M CH ₃ COOH (HAc)	3	-
1M CH ₃ COOLi/CH ₃ COOH (H/LiAc)	4.5	-

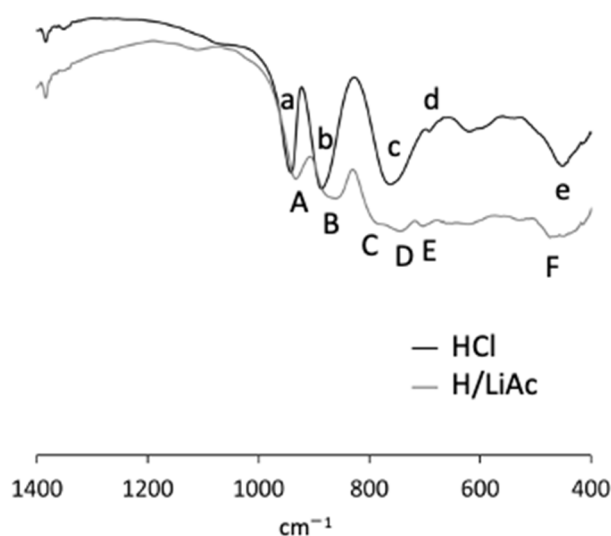


Figure S7. FT-IR spectra of the solid products isolated from the acidification of a solution of **K-CoW₁₂** with aqueous 1M HCl or H/LiAc. The assignment revealed that the solid isolated from the reaction with HCl corresponds to **K-CoW₁₂** (small letters), whereas that from H/LiAc agrees with **K-Co₂W₁₁** (capital letter). Find the detailed band assignment for **K-Co₂W₁₁** and **K-CoW₁₂** in the manuscript enclosed in Figures 2 and 3, respectively.

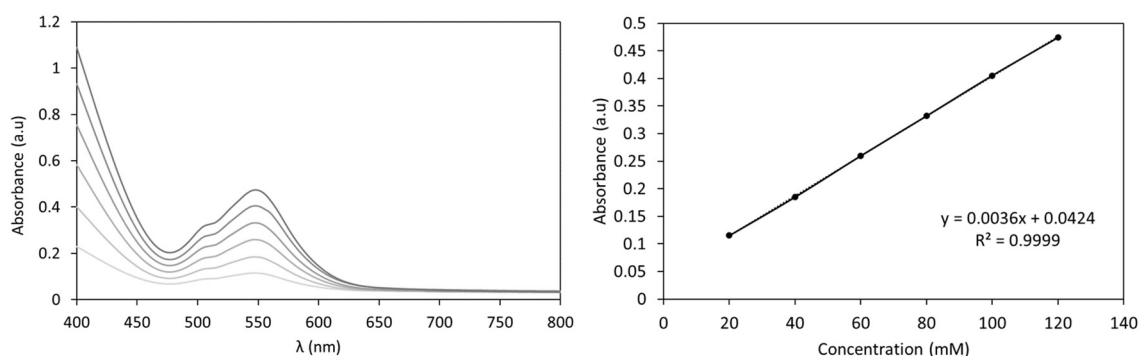


Figure S8. UV-Vis absorption spectra (left) for different concentrations (20–120 mM) in 1M H/LiAc buffer of **K-CoSiW₁₁** prepared following previously reported procedures, together with its calibration curve (right).

References

30. Nolan, A.L.; Burns, R.C.; Lawrance, G.A. Oxidation of $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$ to $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ by Peroxomonosulfate in Strong and Weak Acid Solutions, an Example of Zero-Order Kinetics. *J. Chem. Soc. Dalton Trans.* **1998**, 3041–3048, doi:10.1039/a804598d.
33. Gimenez-Saiz, C.; Galan-Mascaros, J.R.; Triki, S.; Coronado, E.; Ouahab, L. $[(\text{Co}(\text{H}_2\text{O})_4)_2(\text{H}_2\text{W}_{12}\text{O}_{42})]_{\text{N}^{6n-}}$: A Novel Chainlike Heteropolyanion Formed by Paradodecatungstate and Cobalt(II) Ions. *Inorg. Chem.* **1995**, 34, 524–526, doi:10.1021/ic00106a015.
44. Pretsch, E.; Bühlmann, P.; Badertscher, M. *Structure Determination of Organic Compounds: Tables of Spectral Data*; Springer Berlin Heidelberg: Berlin, Heidelberg, 2020; ISBN 978-3-662-62438-8.