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Supporting information for article:

Ab *initio* structure determination of $Eu^{III}5(C2H4O2^{2-})6(CH3CO2^{-})3$ by X-ray powder diffraction

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Material characterization

FTIR spectroscopy was performed on a Bruker Equinos spectrometer in the region 500−4000 cm^{-1} using the well-known KBr technique. The spectra of the as-produced beige powder and the free ethyleneglycol were recorded and compared in Figure S1.

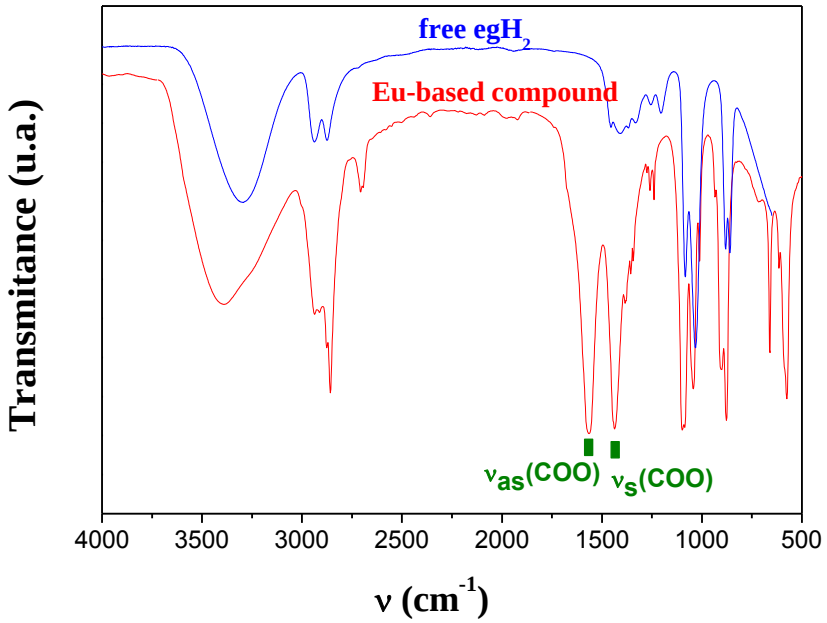

Figure S1. FTIR spectrum recorded on the **as-produced** Eu-based solid precipitate in **ethyleneglycol** (red line) compared to that of the free ethyleneglycol (blue line)

Both exhibit a lot of similitudes. First, the two spectra evidence a large band around 3400 cm^{-1}, which is characteristic of stretching vibration of O-H groups in water and alcohols. They also exhibit two sharp bands at 2850-2950 cm^{-1} usually attributed to the asymmetrical and symmetrical stretching vibrations of the C-H groups. At lower energy, typically at 1050 et 1125 cm^{-1} they evidence deformation vibration bands of C-H groups and stretching vibration bands of C-O and C-C groups in alcohols, and specifically in glycols. [S1,S2] Additional bands appear only in the Eu-based glycolate compound spectrum at 1566-1580 cm^{-1} and 1438-1384 cm^{-1}, respectively. These bands are usually assigned to the asymmetrical ν_{as} and symmetrical ν_{s} stretching vibrations of the COO groups in

[S1] Knetsch D. and Groeneveld W.L. (1973) Alcohols as ligands: Part III Complexes of Ethylene glycol with some divalent metal halides, *Inorganic Chimica Acta* **7**, 81-87.
[S2] Knetsch D. and Groeneveld W.L. (1973) Alcohols as ligands: Part IV. Complexes of ethylene glycol with some metal(II) sulfates and nitrates, *Recueil des Travaux Chimiques des Pays-Bas baner* **92**, 855-864.

carboxylates. [S3] Their observation means that the produced compound does not only contain ethyleneglycol or ethyleneglycolate as organic constituent but also acetate species. Besides, the difference $\Delta\nu = \nu_{as} - \nu_{s}$ is found to be about 130 cm^{-1}, suggesting that the acetate ions are mainly bridging ligand [S3] in the final structure.

^{151}Eu Mossbauer spectroscopy was performed at 5 K in zero-magnetic-field, operating in a transmission geometry and using a ^{57}Co/Rh γ-rays source. The collected spectrum looked like a singlet and was analysed by least squares fitting method using Lorentzian functions (Figure S2). The isomer shift was found to be comprised between 0 and 5 $mm.s^{-1}$, in agreement with non-magnetically interacting trivalent europium cations.

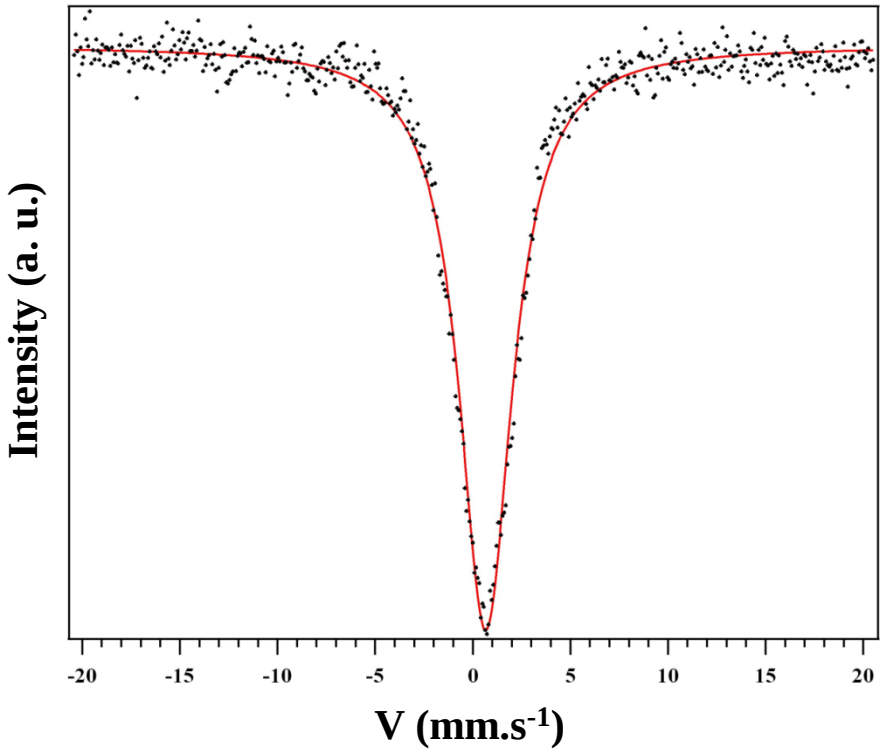

Figure S2. ^{151}Eu Mossbauer spectrum recorded at 5K on the as-produced Eu-based solid precipitate in ethyleneglycol.

To complete our structural investigationses, thermogravimetry was conducted on the fresh powder to quantify its organic componentweight content. A Setaram TGDTA-92 thermobalance was used, heating the samples from 20 to 800 °C (5 °C.min^{-1}) in air. The recorded weight loss and heat flow variations as a function of the temperature are given in Figure S3.

[S3] Nakamoto K., *Infrared Spectra of inorganic and coordination compounds*, John Wiley & Sons Inc, 4th edn (1993).

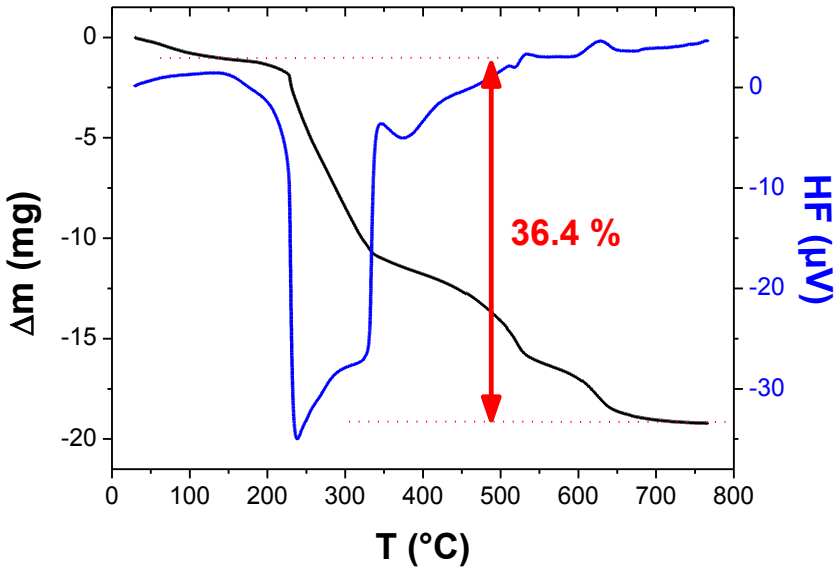

Figure S3. The variation of the weight loss (in black) and the heat flow (in blue) as a function of the temperature as measured on the as-produced Eu-based solid precipitate in ethyleneglycol.

A total weight loss of 36.4 wt.-% was observed between 200 and 700°C. It is very probably associated to the departure of the ethyleneglycolate and acetate species associated to two exothermic heat flow peaks, and corresponding to the complete decomposition of the polymeric Eu-based complex and leading to the formation of the Eu_2O_3 oxide as confirmed by XRD analysis of the final product.

Structural details

The geometry of eg^{2-} ligand was optimized for the studied structure. Two stable conformations were obtained (Figure S4).

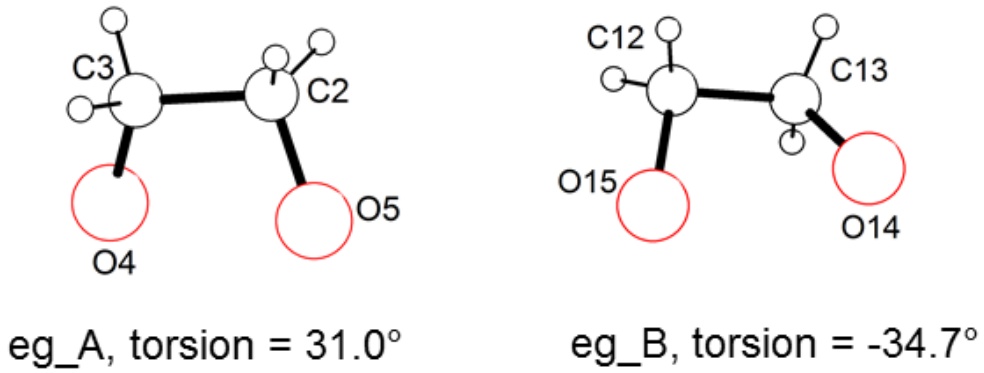

Figure S4

Representation of the two geometrically optimized eg^{2-} anion and designated as “eg_A” (left) and “eg_B” (right) in the maintext. O and C atoms are in red and black, respectively.

Finally, the atomic coordinates and temperature factors of the refined structure are reported in Table S1.

Table S1. Atomic coordinates and temperature factors of the refined structure for the as-produced Eu-based solid precipitate in ethyleneglycol.

Atom	x	y	z	Ueq (Å^2)
Eu1	0.08552(5)	0.89895(5)	0.99515(5)	0.0450(3)
Eu2	0.13950(5)	0.88951(5)	0.87500	0.0494(6)
Eu3	0.00000	0.00000	0.00000	0.0460(10)
C2	0.0685(7)	0.0289(4)	0.8082(3)	0.026(3)
H2A	0.03840	0.01333	0.80632	0.02596
H2B	0.09279	0.00621	0.80331	0.02596
C3	0.0713(6)	0.0671(4)	0.7726(4)	0.026(3)
H3A	0.08312	0.05411	0.74357	0.02596
H3B	0.04020	0.07885	0.76639	0.02596
O4	0.1005(4)	0.1054(4)	0.7860(4)	0.026(3)
O5	0.0736(4)	0.0514(4)	0.8515(3)	0.026(3)
C6	0.0651(8)	0.7565(4)	0.9322(7)	0.074(4)
H6A	0.09267	0.74190	0.91897	0.07530
H6B	0.03989	0.75309	0.91059	0.07530
H6C	0.05767	0.74135	0.96087	0.07530
C7	0.0751(6)	0.8088(4)	0.9407(7)	0.074(4)
O8	0.0474(4)	0.8304(4)	0.9710(4)	0.074(4)
O9	0.1135(4)	0.8306(5)	0.9216(5)	0.074(4)
C12	0.0198(4)	0.9164(4)	0.8947(7)	0.057(3)
H12A	0.00441	0.90075	0.91693	0.05637
H12B	0.02394	0.89679	0.86787	0.05637
C13 -	0.9597(3)	0.8822(5)	0.057(3)	0.0060(6)
H13A	0.00361	0.97015	0.85122	0.05637
H13B -	0.95472	0.88212	0.05637	0.03637
O14	0.0072(5)	0.9958(4)	0.9166(4)	0.057(3)
O15	0.0652(3)	0.9327(5)	0.9129(4)	0.057(3)