

Electronic Supplementary Information

Cooperative reduction by Ln²⁺ and Cp*⁻ ions: synthesis, structure, and magnetic properties of Sm, Eu, and Yb complexes with 3,6-di-*tert*-butyl-*o*-benzoquinone

Nikolay A. Pushkarevsky,^{*a,b} Mikhail A. Ogienko,^a Anton I. Smolentsev,^a Igor N. Novozhilov,^a Alexander Witt,^c Marat M. Khusniyarov,^c Vladimir K. Cherkasov,^{d,e} and Sergey N. Konchenko^{a,b}

* To whom correspondence should be addressed.

^a *Nikolaev Institute of Inorganic Chemistry, Siberian Division of RAS, Akad. Lavrentieva str. 3, 630090 Novosibirsk, Russia. E-mail: nikolay@niic.nsc.ru*

^b *Department of Natural Sciences, Novosibirsk State University, Pirogova Street 2, 630090 Novosibirsk, Russia.*

^c *Department of Chemistry and Pharmacy, Friedrich-Alexander-University of Erlangen-Nuremberg, Egerlandstr. 1, 91058 Erlangen, Germany.*

^d *G. A. Razuvaev Institute of Organometallic Chemistry of RAS, Tropinina St. 49, 603950 Nizhny Novgorod, Russia.*

^e *N. I. Lobachevsky Nizhny Novgorod State University, Gagarin Ave., 23, 603950, Nizhny Novgorod (Russia).*

Elemental analysis of the pale-grey by-product from the Eu reaction shows the following composition:

C 50.3 H 6.3% (averaged)

For the formula $[\text{Eu}(\text{dbcat})(\text{thf})]_n$, the values should be C 48.65, H 6.35%; for the formulas with remained Cp* ligands one would expect noticeably higher carbon content, *e. g.* for the formula $[\text{Eu}(\text{dbcat})\text{Cp}^*]$ C 56.80, H 6.95%. Any compound of Eu^{III} with only dbcat, Cp*, and THF ligands would also possess much higher carbon content. Moreover, the presence of Cp* ligands would result in coloured complexes, rather than nearly colourless, as we observed. For comparison, the soluble product obtained in the reaction of EuI₂ with K₂(dbcat) in THF was yellow (for this reaction, both reagents were obtained by reacting excess of corresponding metal with I₂ or dbbq in THF in separate schlenk tubes prior to combining). Hence, we expect the pale-grey by-product to be neither a simple europium catecholate of the formula $[\text{Eu}(\text{dbcat})(\text{thf})]_n$ ($n = 1$ or 2), nor a Eu^{III} catecholate species, although the by-product and the yellow Eu(II) catecholate have very close IR spectra (see below). All attempts to crystallize this compound from pentane or hexane led to polycrystalline material, where crystals could be distinguished under the microscope, but were too small for X-ray crystallographic analysis.

IR spectroscopy

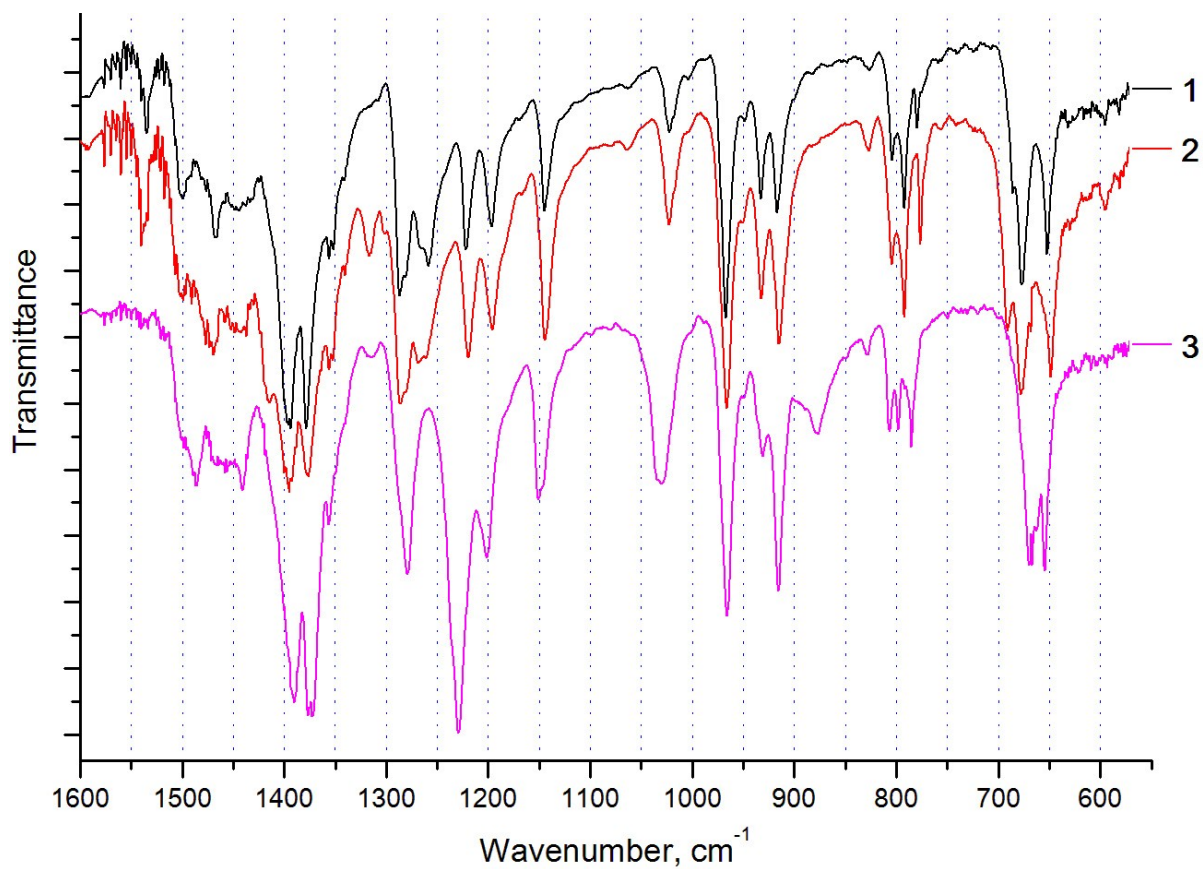


Figure S1. IR spectra of the complexes **1**, **2**, and **3**.

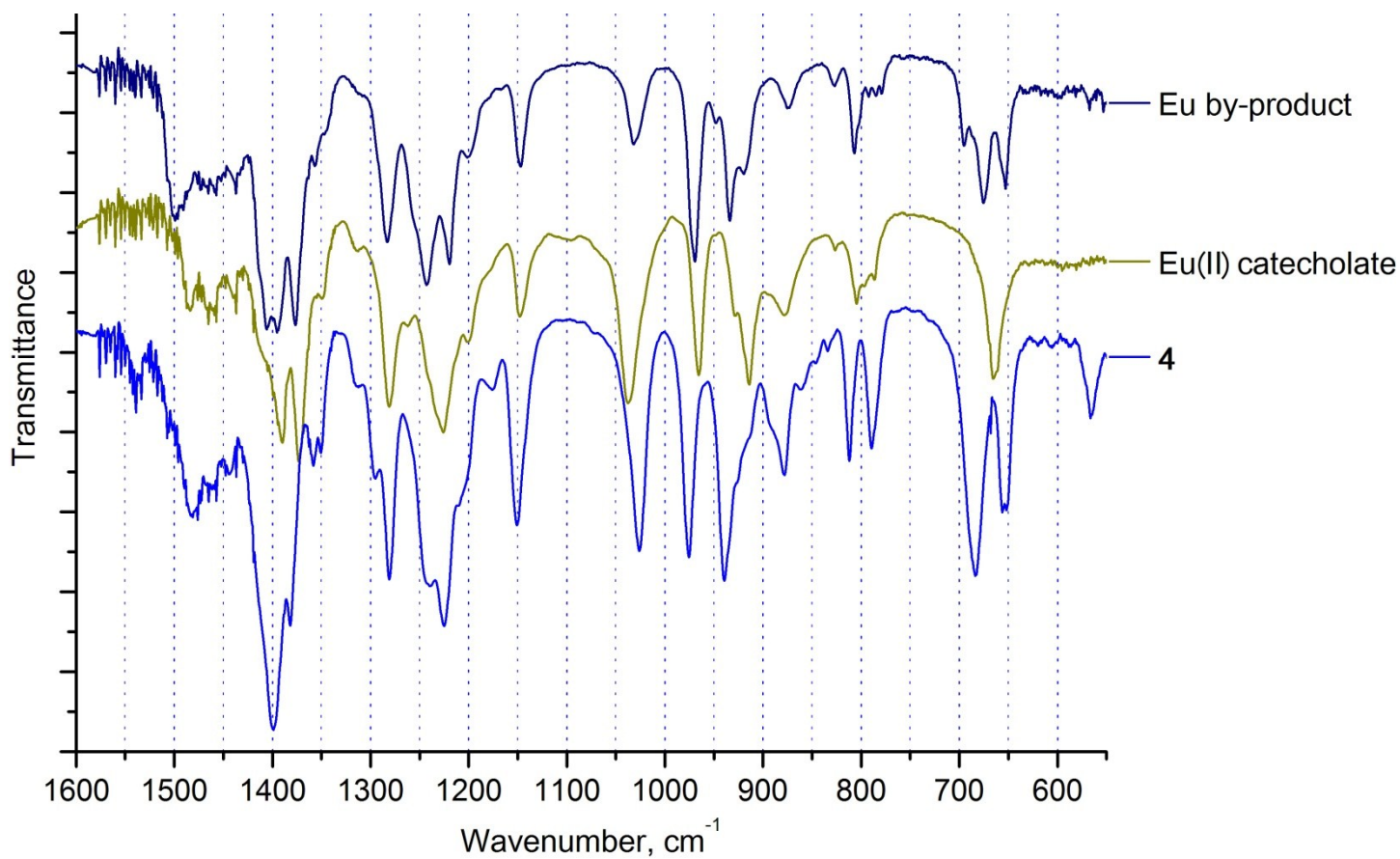


Figure S2. IR spectra of the complex **4** and the pale-grey by-product from the Eu reaction.

Magnetic measurements

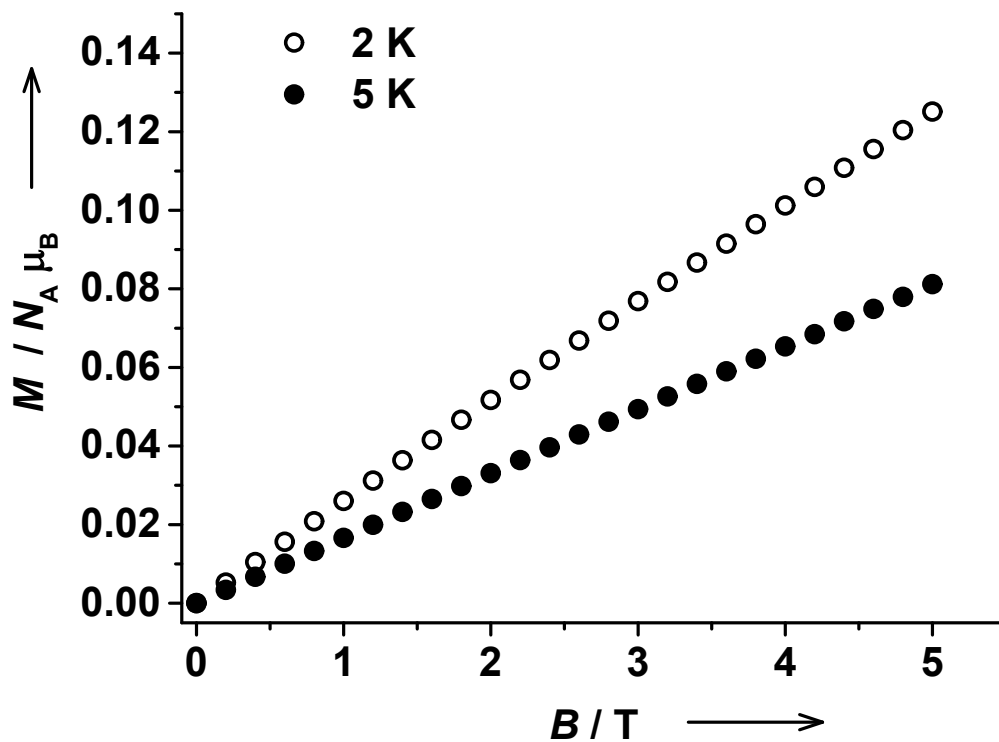


Figure S3. Field-dependent magnetization of 1 measured at 2 and 5 K.

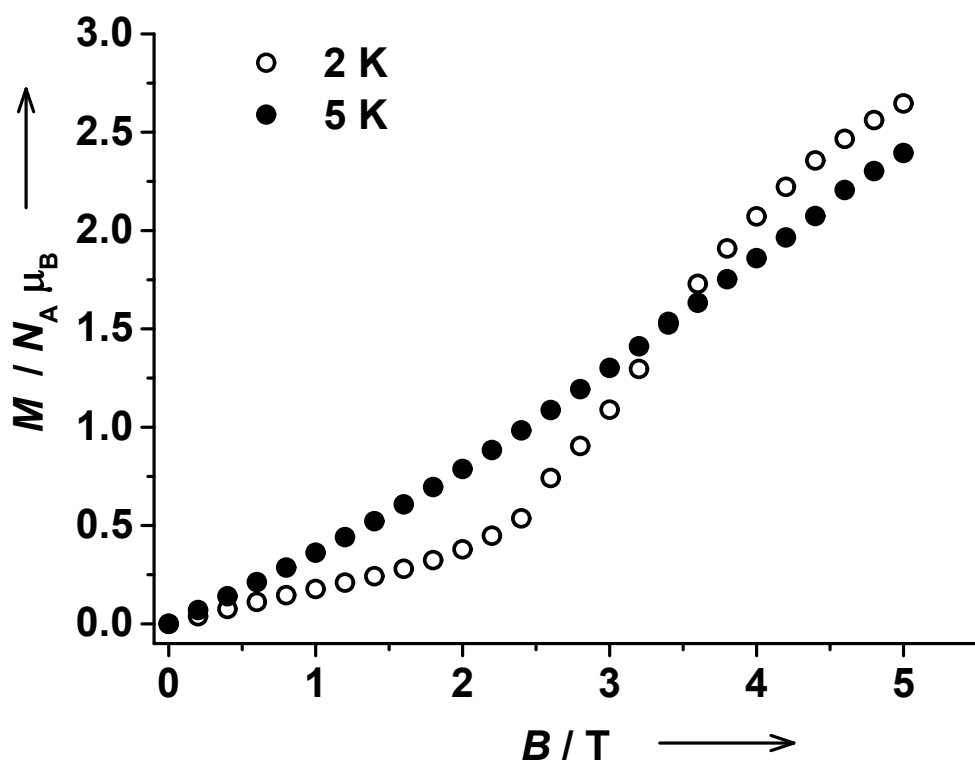


Figure S4. Field-dependent magnetization of **2** measured at 2 and 5 K. The intersection of two field-dependent curves (S-shape) is likely due to an antiferromagnetic ground state.¹

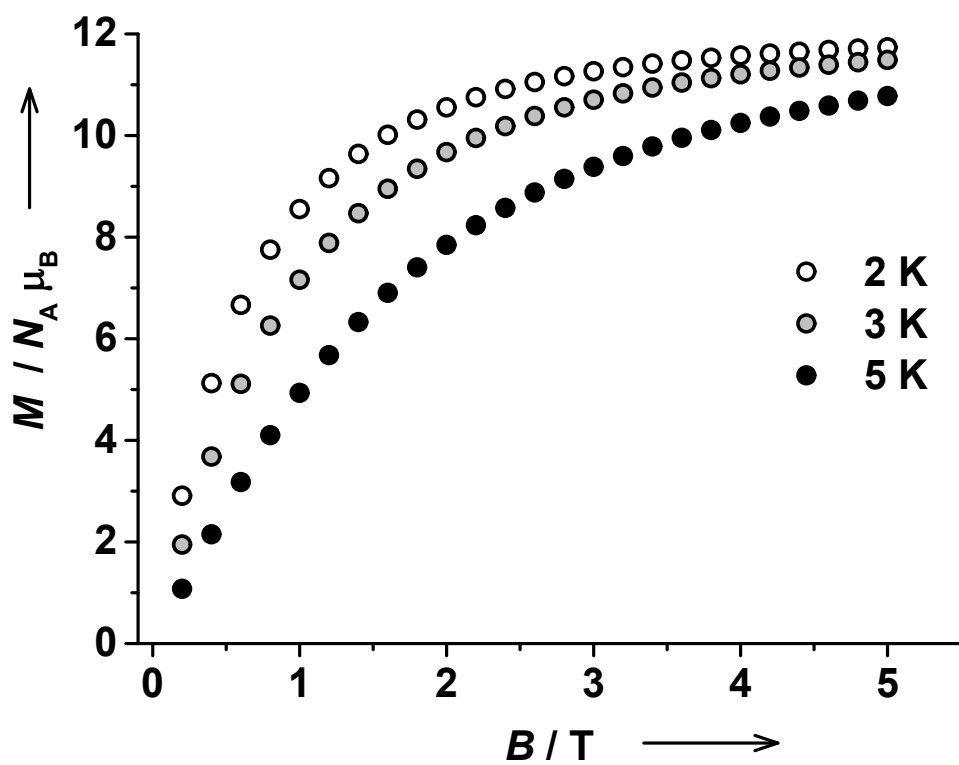


Figure S5. Field-dependent magnetization of **3** measured at 2, 3 and 5 K.

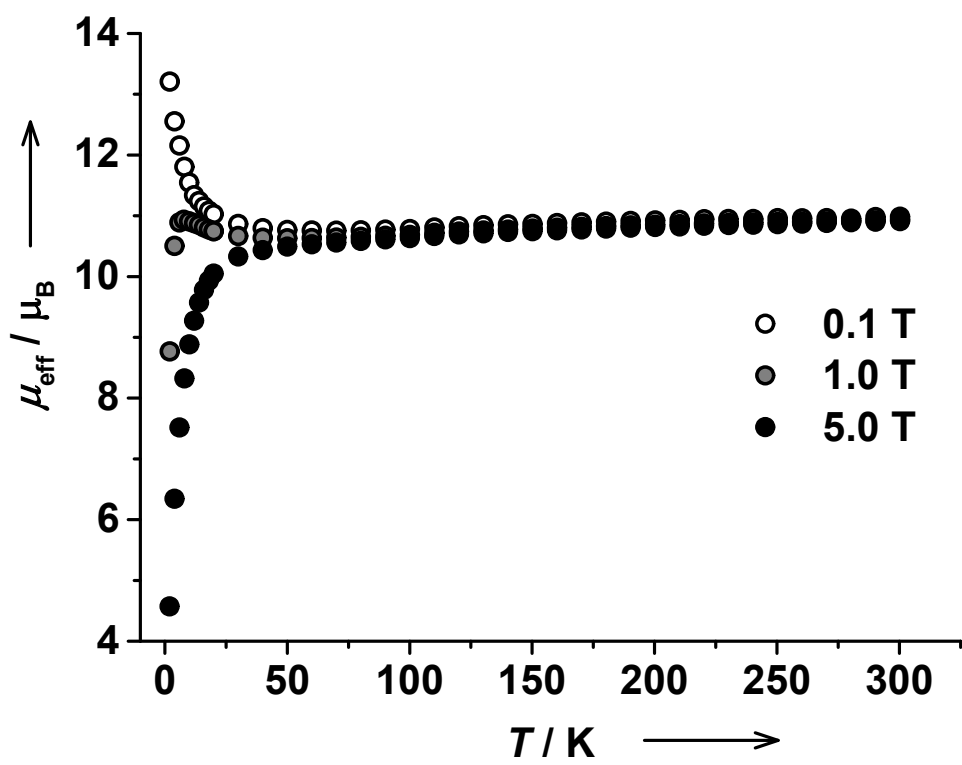


Figure S6. Variable-temperature effective magnetic moment of **3** measured at external magnetic field 0.1, 1.0 and 5.0 T.

Reference

1. K. S. Pedersen, M. Sigrüst, M. A. Sørensen, A.-L. Barra, T. Weyhermüller, S. Piligkos, C. A. Thuesen, M. G. Vinum, H. Mutka, H. Weihe, R. Clérac and J. Bendix, *Angew. Chem. Int. Ed.*, 2014, **53**, 1351–1354.