

Self assembly, structure and properties of the decanuclear lanthanide ring complex, $\text{Dy}_{10}(\text{OC}_2\text{H}_4\text{OCH}_3)_{30}$

L. Gunnar Westin,^{*a} Mikael Kritikos^b and Andrea Caneschi^c

^a Department of Materials Chemistry, Ångström Laboratory, Uppsala University, SE-751 21, Uppsala, Sweden. E-mail: Gunnar.Westin@mkem.uu.se > ; Tel: 46 18 4713740

^b Department of Structural Chemistry, Arrhenius Laboratory, Stockholm University, SE-106 91, Stockholm, Sweden. E-mail: mkr@struc.su.se; Fax: 46 8 163118; Tel: 46 8 161440

^c Dipartimento di Chimica and UdR INSTM di Firenze, Polo Scientifico, Università di Firenze, 50019 Sesto Fiorentino (Fi), Italy. E-mail: andrea.caneschi@unifi.it; Tel: 39 0554573327

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Self assembly produced high yields of the lanthanide ring complex $\text{Dy}_{10}(\text{OC}_2\text{H}_4\text{OCH}_3)_{30}$, the largest lanthanide ring known, characterized by X-ray diffraction methods and by magnetic susceptibility as a function of temperature.

Ring complexes form a class of compounds that have received much interest during recent years, and presently a number of these intriguing and beautiful complexes are known, including several examples of large ring systems of more than 10 of Cr, Fe or Ni atoms.¹ In fact, depending on the nature of the exchange interaction, these rings can behave as Single Molecule Magnets, exhibiting slow dynamics of the magnetization and quantum tunneling when characterized by ferromagnetic interaction^{2a} or, in the opposite case, as molecular analogues of nano-scale antiferromagnets, for which tunneling effects have been also predicted.^{2b,2c} However, there are very few reported ring complexes of lanthanide elements, and so far the larger ring structures found for the 3d elements are lacking.³ The appearance of ring complexes, especially considering the large number of metal atoms often constituting the structures, makes their stability and formation mechanism highly interesting but also challenging to elucidate, since most of the rings have been obtained in limited yield and in coexistence with other polynuclear compounds. Controlling the synthesis and understanding the properties of these unique structures has an impact on the future manufacture of nano-devices based on electronic, magnetic or optic properties related to well-defined molecular units. Moreover, rare-earth ions have long been exploited to influence the properties of magnets by introducing anisotropic contributions and by changing the compensation temperature.⁴ Little is known about the general nature of the exchange interactions of 4f ions among themselves and with magnetic centres, because few simple products containing magnetically coupled rare-earth ions have been available until recently.

The $\text{Dy}_{10}(\text{OC}_2\text{H}_4\text{OCH}_3)_{30}$ (**1**) ring reported here is not only one of very few lanthanide ring complexes, but it is also the largest lanthanide ring obtained as far as we know, showing that large rings occur also for the lanthanides even with simple oxygen donor ligands without template effects. It self-assembles and crystallizes as the sole soluble complex by two different routes, indicating that these rings are stable. Therefore, these systems should be quite valuable for the understanding of ring formation.

The synthesis was made in two ways: (i) By dissolving metal chips in methoxy-ethanol (MOEH)-toluene with the aid of an HgCl_2 catalyst, by analogy with the synthesis reported for the corresponding Y_{10} rings.⁵ The reaction can be described as: $20 \text{ Dy} + 30 \text{ MOEH} \rightarrow 10 \text{ DyH}_{3-x} + \text{Dy}_{10}(\text{MOE})_{30} + 5x \text{ H}_2$. (yield of **1** 50%) (ii) Metathesis of $30 \text{ K}(\text{MOE}) + 10 \text{ DyCl}_3 \rightarrow \text{Dy}_{10}(\text{MOE})_{30} + 30 \text{ KCl}$. The methathetic route to Ln alkoxides has often been reported as not going to completion, and thus yielding impure products, but we obtained a pure and completely crystallizable product in ca 90–95% yield. Although the $\text{Y}_{10}(\text{MOE})_{30}$ ring was reported over a decade ago, attempts

to synthesize the corresponding Ln-methoxy-ethoxides in the same way seem always to have resulted in isolation of condensed three-dimensional oxo-alkoxide clusters, and therefore the present results are somewhat unexpected.^{6,7} The solid-state structure of **1** was revealed by single-crystal X-ray crystallography, and the molecular structure is shown in Fig 1. The centrosymmetric cyclic unit consists of ten Dy atoms connected by the O-alkoxo donor atoms of the MOE ligands. All Dy atoms exhibit irregularly shaped seven-coordinated DyO_7 entities composed of 5 alkoxo oxygens (one O from a terminal MOE group and four from bridging groups) and 2 ether oxygens (both non-bridging). The Dy–O bond distances increase in the order: Dy–O(terminal alkoxo) (2.11 to 2.12 Å) < Dy–O(bridging alkoxo) (2.27 to 2.34 Å) < Dy–O(ether) (2.52 to 2.58 Å). The same trend in the metal–oxygen distances was observed in the related $\text{Y}_{10}(\text{MOE})_{30}$.⁵ The Dy atoms form the ring structure by sharing alkoxo oxygen atoms in double bridges with the Dy–O–Dy angles in the range of 109.1–112.6°. The distances between two neighboring Dy centers that are linked by the alkoxo bridges are in a narrow range of 3.79–3.81 Å. An indication of the ring size is given by the distances between symmetry equivalent Dy atoms, which are in the range 11.58 to 11.98 Å. Furthermore, the conformation adopted by the ten-membered metal ring skeleton is non-planar, with a crown type conformation. The organic shell encapsulating the inner metal–oxygen core prevents formation of intermolecular polar contacts and the rings seem to be bound to each other mainly by relatively weak van der Waals forces. Structurally characterized Ln-methoxy-ethoxide complexes are scarce in the literature. To our knowledge, the oxo-alkoxides $\text{Gd}_6\text{O}(\text{MOE})_{16}$ and $\text{Pr}_8\text{O}(\text{MOE})_{16}(\text{OPMe}_3)_4$ are the only representatives.^{6,7} It can also be mentioned that a wheel structure has been determined for the oxo-methoxy-ethoxide $\text{Mn}_{19}\text{O}_{12}(\text{MOE})_{14}(\text{MOEH})_{10}^*(\text{MOEH})$, making this simple ligand interesting for the synthesis of wheel and ring structures.⁸

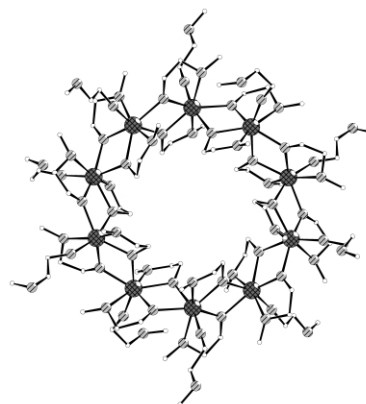


Fig. 1 Structure of the $\text{Dy}_{10}(\text{MOE})_{30}$ ring.

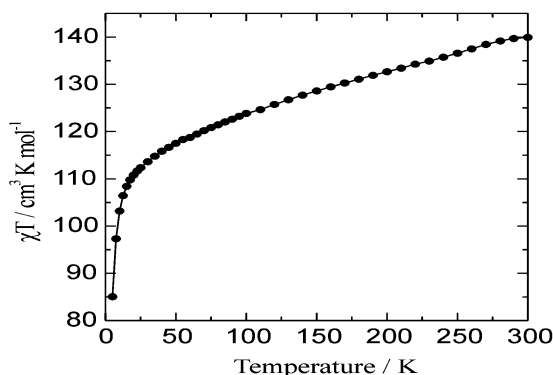


Fig. 2 χT vs. T behavior of $\text{Dy}_{10}(\text{MOE})_{30}$.

It is well known that for systems containing Ln ions the effects of the exchange coupling are much weaker than with transition metal ions, because the f orbitals are less extended than d orbitals. Furthermore, in these ions (if $\text{Ln} \neq \text{Gd}$) the analysis of effects due to exchange gives rise to additional difficulties, since the strength of these interactions is comparable with that of the crystal field acting on the ion, due to the large orbital contribution. As a consequence, the disentanglement of the single-ion magnetic anisotropy from the exchange contribution in the analysis of the temperature dependence of the magnetic susceptibility is a largely unachieved task, especially for highly anisotropic ions like Dy^{3+} , and only empirical approaches are found in the literature. This compound shows room temperature χT values of about $138 \text{ emu mol}^{-1} \text{ K}$, in good agreement with what may be expected on the basis of literature data for ten free Dy^{3+} ions: 140 emu mol^{-1} .⁹ The χT values decrease with decreasing temperature, a phenomenon that should be attributed to crystal field effects rather than to exchange coupling. The fact that the curve is not flat at room temperature indicates that its multiplet width is very large, and its various levels cannot be considered as equally populated; this ion is indeed known to be among the most anisotropic of the whole lanthanide series. The χT vs. T plot is reported in Figure 2. The magnetization vs. field curve rapidly reaches a saturation of about $48 \mu_{\text{B}}$ at 3 T and 2 K, further suggesting that the exchange effects should be small for this compound. Accordingly, any weak exchange interaction within the ring is masked by crystal field effects, and no conclusions can therefore be drawn about its value and sign for this product.

In summary, the first Ln_{10} ring has been found; it is the largest reported Ln ring as well as one of the very few characterized Ln rings or wheels. The crown-shaped ring was obtained by simple self-assembly syntheses, starting with the metal or the metal chloride and producing yields of 1 in ca 50 and 90–95%, respectively. † It was the only soluble compound, making isolation easy. The magnetic behavior of this Dy^{3+} derivative is in full agreement with the expected behavior; better insight concerning the value and sign of the exchange coupling inside the ring might be obtained by analysis of the less anisotropic 4f ions.

Notes and references

† *Synthesis of $\text{Dy}_{10}(\text{MOE})_{30}$ (1)*: All synthesis procedures were carried out in a glove box in dry oxygen-free argon atmosphere, and all glass equipment was dried at 150°C . The solvents were dried by distillation with CaH_2 . (i) Dysprosium chips (1.732 g, 10.66 mmol) were added ca 0.3 mg of HgCl_2 and 20 ml MOEH:toluene (1:1 vol:vol) and heated to $70\text{--}80^\circ \text{C}$. After 24–48 hours, the mixture was centrifuged to sediment the olive-green finely divided DyH_{3-x} solid. The pale yellow solution part was transferred to another flask and evaporated in vacuum, leaving a very moisture-sensitive crystalline or sticky solid of $\text{Dy}_{10}(\text{MOE})_{30}$. (ii) Potassium (0.625

g, 16.0 mmol) was dissolved in 20 ml MOEH:toluene (1:2 vol:vol) and DyCl_3 (1.433 g, 5.328 mmol) was added. After 48 hours stirring, the mixture was centrifuged to separate KCl and the solution was evaporated, leaving solid $\text{Dy}_{10}(\text{MOE})_{30}$. Crystallization was slow. The UV-vis-NIR and IR spectra of the product obtained by the two procedures were identical. Magnetic measurements were performed with an Oxford Instruments VSM apparatus operating between 0 and 12 T in the temperature range $1.5\text{--}320 \text{ K}$. The compound was charged in the sample holder, weighed in a dry oxygen-free glove box, and transferred to the VSM instrument avoiding air contact.

Crystal data for 1: $\text{C}_{90}\text{H}_{210}\text{Dy}_{10}\text{O}_{60}$: $M = 3877.59$ Monoclinic space group $P2_1/c$ (No. 14), $a = 13.669(2)$, $b = 20.390(2)$, $c = 24.851(3) \text{ \AA}$, $\beta = 95.22(2)^\circ$, $V = 6897.4(14) \text{ \AA}^3$, $Z = 2$, $T = 170 \text{ K}$, $D_c = 1.867 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 5.43 \text{ mm}^{-1}$, $F(000) = 3780$, 43591 reflections measured, 10837 unique ($R_{\text{int}} = 0.0877$), 9043 observed ($I > 2\sigma(I)$), 723 parameters refined, absorption correction (numerical): $T_{\text{min}}/T_{\text{max}} = 0.350/0.560$. $R1 = 0.0596$, ($I > 2\sigma(I)$), $wR(F^2) = 0.1147$, $S = 1.11$ (all data). Max./min. residual electron density: $2.15\text{--}1.87$. Data collection: STOE-IPDS image plate diffractometer using $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The numerical absorption correction was performed with the programs X-RED and X-SHAPE. The structure was solved by direct methods and refined by a full-matrix least-squares procedure on F^2 . Hydrogen atoms were included at calculated positions, riding on the carbon atoms. ‡

‡ CCDC 194816. See <http://www.rsc.org/suppdata/cc/b3/b300237c/> for crystallographic data in .cif or other electronic format.

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