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Synthesis and crystal structure of the first d–f heterodinuclear Dy(III)–Cu(II) cryptate

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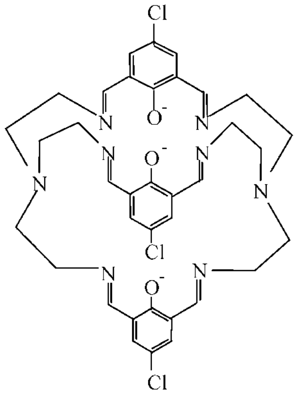
The heterodinuclear cryptate [DyCuL(DMF)](ClO_4)$_2$·MeCN [where L denotes the deprotonated anionic cryptand obtained by condensation of tris(2-aminoethyl)amine with 2,6-diformyl-4-chlorophenol] has been obtained by a stepwise method; the presence of copper(II) and dysprosium(III) in the cavity of the cryptand was evidenced by X-ray structure analysis and ESMS spectroscopy.

Heterodinuclear complexes have received much attention owing to their electronic, electrochemical, and magnetic properties arising from the metal–metal interaction,[1] and mimicking of the active centers of some metalloenzymes, for example, copper–zinc superoxide dismutase,[2] cytochromic oxidase,[3] hydrogenase,[4] *etc.* Heterodinuclear complexes of dinucleating ‘Robson-type’ macrocycles[5] have been recognized for many years.[6] Most of these are two-dimensional macrocyclic complexes encapsulating transition metal ions. A few d–f heteronuclear macrocyclic complexes have been reported.[7] Since it was found that the Gd(III)–Cu(II) intramolecular interaction in the complexes is ferromagnetic,[8] interest has been aroused in the synthesis of d–f heteronuclear macrocyclic complexes in order to develop new functions. The cryptates have good thermodynamical stability and kinetic inertness toward metal dissociation. The first homodinuclear lanthanide cryptate was synthesized in 1999,[9] but up to date no examples of heteronuclear d–f cryptates have been described in the literature. Here, we report the first example of a d–f heteronuclear Dy(III)–Cu(II) complex of a Robson-type cryptand together with its crystal structure. The mononuclear dysprosium cryptate was synthesized by metal-templated reaction between 2,6-diformyl-4-chloro-phenol (dcp) and tris(2-aminoethyl)-amine (tren) in the presence of hydrated dysprosium nitrate in 3 : 2 : 1 mol ratio in absolute methanol. After refluxing for 3–4 h, the yellow mononuclear dysprosium cryptate was produced, which was used as a precursor to synthesize the heteronuclear complex. The yellow complex (117 mg, 0.1 mmol) was dissolved in methanol (20 cm^3) containing a small amount of DMF. The pH of the solution was *ca.* 6. After adding an excess of CaH_2 powder, the pH of the solution changed to 7–8. After filtering the solution, copper perchlorate (0.1 mmol) in methanol (5 cm^3) was added resulting in a green solution. After refluxing for *ca.* 2 h a red solid was produced. Slow diffusion of diethyl ether into an acetonitrile solution of the complex gave red prismatic crystals of [DyCuL(DMF)](ClO_4)$_2$·MeCN suitable for an X-ray study,†‡ where L is the deprotonated anionic cryptand obtained by condensation of tren with dcp (Scheme 1).



Scheme 1 Anionic cryptand L.

The ESMS spectra display intense peaks corresponding to the fragments [DyCu(L − 3Cl)(DMF)(MeCN)]$^{2+}$ (100), [DyCu(L − 3Cl)(DMF) + (Cl^-) + 2(MeOH)]$^+$ (42) and [DyCu(L − 3Cl)(DMF) + (Cl^-) + 2(MeOH) + (MeCN)]$^+$ (24%), confirming the presence of the Dy(III)–Cu(II) core in the cryptate. It is found that the chlorine atom of the phenyl rings can be lost under ESMS conditions, whereas the Dy(III)–Cu(II) macrobicycle remained intact and [DyCu(L − 3Cl)(DMF)(MeCN)]$^{2+}$ appears with 100% base peak intensity.

Structural analysis of this complex comfirmed the presence of the Dy(III)–Cu(II) unit in the cavity of the macrocycle. The crystals contain the cation [DyCuL(DMF)]$^{2+}$, two independent perchlorate anions and an acetonitrile molecule. Fig. 1 illustrates the structure of the cation.

The Dy(III) ion is located at one end of the cavity and is eight coodinated with the bridgehead nitrogen atom [N(1)], three imino-nitrogen atoms [N(2), N(3), N(4)], the three μ-phenolate oxygen atoms [O(1), O(2), O(3)] and the oxygen atom O(4) of DMF. The coordination polyhedron is best described as distorted dodecahedral. The Dy–N(imino) distances are in the range 2.443–2.509 Å, with Dy(III)–N(1) 2.617 Å, shorter than found in a Dy(III) mononuclear cryptate reported by Fenton and coworkers,[10] however the Dy(III)–O(phenolate) distances are longer than those reported in the literature.[10] The other end of the cavity is occupied by the Cu(II) ion. Three μ-phenolate oxygen and three imino-nitrogen atoms coodinate to Cu(II), forming a distorted octahedron. The Dy···Cu distance is

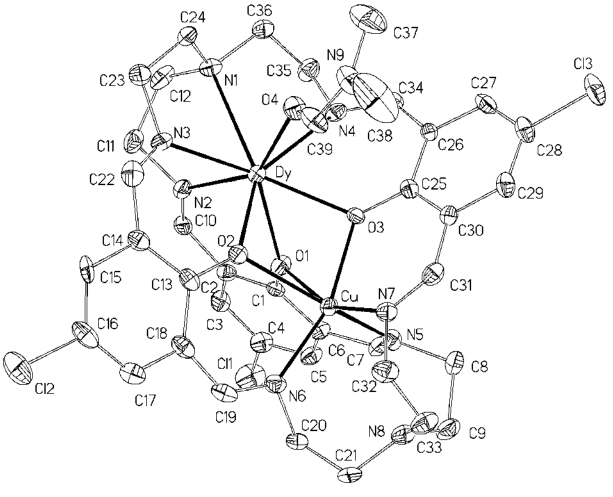


Fig. 1 Crystal structure of [DyCuL(DMF)]$^{2+}$.

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3.255 Å. The Dy(III)–O(1)–Cu(II), Dy(III)–O(2)–Cu(II) and Dy(III)–O(3)–Cu(II) angles are 92.1, 90.0 and 97.1°, respectively. The distance between the two bridgehead nitrogens, N(1)···N(8) 9.003 Å, is larger than that found for a mononuclear dysprosium(III) cryptate (8.361 Å)[10] or in a homobinuclear Lu(III) cryptate (8.65 Å),[9] and slightly shorter than that in $[Cd_2L]^{2+}$ (9.01 Å),[11] revealing that the cryptand (L) can expand or contract as appropriate to encapsulate one or two metal ions.

Previously we have described a mononuclear neodymium(III) cryptate of ligand L in which one water molecule was encapulated as a guest.[12] In the present work we have extended the work *via* a stepwise synthesis to introduce a 3d metal ion which occupies the position of the water molecule in the cavity. Further d–f heteronuclear cryptates consisting of transition metals [copper(II), nickel(II), *etc.*] and other lanthanide ions have also been synthesized and will be reported elsewhere.

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Notes and references

† $[DyCuL(DMF)](ClO_4)_2{\cdot}MeCN$ yield 40% (Found: C, 38.20; H, 3.75; N, 10.45; $C_{41}H_{46}Cl_5N_{10}O_{12}CuDy$ requires: C, 38.65; H, 3.64; N, 10.99%). λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) (MeCN) 245(75 214), 380(14 511) 490(402). ν_{max}(KBr)/cm^{-1} 1650s(C=N), 1540s(C–O) and 1097(ClO_4^-). Λ_m(DMF, 298 K): 150 s cm^2 mol^{-1}. The complex is soluble in methanol, acentonitrile and DMF.

‡ *Crystal data*: $[DyCuL(DMF)](ClO_4)_2{\cdot}MeCN$, $C_{41}H_{46}Cl_5N_{10}O_{12}CuDy$, M = 1274.17; red prism, 0.28 × 0.16 × 0.06 mm, monoclinic, space group $P2_1/c$, a = 19.6358(7), b = 11.8049(4), c = 21.5544(8) Å, β = 98.2600(3)°, V = 4944.4(3) Å^3, Z = 4, D_c = 1.712 Mg m^{-3}, μ = 2.270 mm^{-1}. Using Mo-Ka radiation (λ = 0.71073 Å) at 293(2) K, a total of 17 965 reflections was collected (1.05 < θ < 25.05°), of which 8693 were independent. Refinement converged to R_1 = 0.0658, wR_2 = 0.1109 [$I > 2\sigma(I)$] and R_1 = 0.1570, wR_2 = 0.1450 (all data).

CCDC 182/1622. See http://www.rsc.org/suppdata/cc/a9/a909926n/ for crystallographic files in .cif format.

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