

Synthesis and structure of a novel carboxylate-bridged heterometallic copper(II)–gadolinium(III) complex

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A novel pentanuclear copper(II)–gadolinium(III) complex has been synthesized and shown by X-ray crystallography to contain a linear array structure connected by chloroacetate bridges.

Polynuclear mixed-metal complexes are of special current interest in relation to the nature of magnetic exchange interactions between transition and rare-earth metal ions through bridging ligands.^{1,2} They are also considered as possible precursors in the production of high temperature superconductors.³ Although metal carboxylate chemistry has a very long history, our understanding of the chemistry of carboxylate-bridged heteronuclear complexes is very limited.⁴ Recently carboxylate-bridged heterodinuclear transition-metal complexes containing multidentate ligands have been investigated with respect to their role in biological systems.⁵ Several other heterometallic Zn^{II}–M^{III} (M = Mn, Co, Ni, etc.)⁶ and Cu^{II}–M (M = Li^I, Mg^{II}, Ca^{II} or Rb^I)⁷ carboxylate complexes have also been structurally characterized, in which the metal centres are bridged uniquely by carboxylate groups.

We have recently synthesized some interesting Cu^{II}₁₂Ln^{III}₆ (Ln = lanthanoid) clusters containing carboxylate bridges of zwitterionic pyridinioacetate and hydroxy bridges⁸ as well as a dinuclear Cu^{II}Ln^{III} compound containing pyridinioacetate.⁹ We now report the first pentanuclear Cu^{II}–Ln^{III} complex bridged only by carboxylate ligands, namely [Cu₃Gd₂(O₂CCH₂Cl)₁₂·(H₂O)₈]·2H₂O **1**.

Complex **1** was synthesized by the self-assembly of Cu^{II} and Gd^{III} ions with chloroacetate. An aqueous solution (2 cm³) of chloroacetic acid (0.57 g, 6.0 mmol) was adjusted to pH ca. 3 by addition of 2 mol dm^{−3} NaOH solution. The salt Cu(NO₃)₂·3H₂O (0.24 g, 1.0 mmol) was added with stirring at 60 °C for 10 min and followed with aqueous Gd(NO₃)₃ (2.0 mmol). The resulting blue solution was adjusted to pH ca. 3.5 and allowed to stand in air at room temperature for 10 d, yielding deep blue prismatic crystals of **1** (60% yield).†

X-Ray crystallography‡ has established that complex **1**

† Found: C, 15.90; H, 2.25. Calc. for C₂₄H₄₄Cl₁₂Cu₃Gd₂O₃₄ **1**: C, 16.00; H, 2.45%. IR data (ν/cm^{−1}): 3367s (br), 3015w, 2959w, 1672vs, 1616vs, 1405vs (br), 1257s, 1145w, 1117w, 1089w, 934w, 793m, 716m, 688m, 625w and 582w.

‡ Crystal data for complex **1**: C₂₄H₄₄Cl₁₂Cu₃Gd₂O₃₄, *M*_r = 1807.11, monoclinic, space group *P*₂₁/*c*, *a* = 10.521(2), *b* = 18.024(4), *c* = 15.310(3) Å, β = 99.85(3)°, *U* = 2860.4(10) Å³, *Z* = 2, *D*_c = 2.098 g cm^{−3}, μ = 4.033 mm^{−1} crystal size 0.30 × 0.40 × 0.25 mm. Data collection (2 ≤ θ ≤ 26.5°) was performed at 294 K on a CAD4 diffractometer, λ(Mo-Kα) = 0.710 69 Å. The structure was solved by direct methods and refined by full-matrix least squares (SHELXL 93)¹⁰ to final wR2 = [Σw(*F*_o² − *F*_c²)/Σw(*F*_o²)]^{1/2} = 0.1804 for 358 parameters and all 6194 unique reflections and conventional R1 = 0.0551 with the weighting scheme *w* = 1/[σ²(*F*_o) + (0.1000*P*)²] where *P* = (*F*_o² + 2*F*_c²)/3; an empirical absorption correction was applied.¹¹ Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/36.

consists of a centrosymmetrical pentanuclear [Cu₃Gd₂(O₂C-CH₂Cl)₁₂(H₂O)₈] molecule, as shown in Fig. 1. Each terminal Cu^{II} atom is co-ordinated by four carboxy oxygen atoms at the basal plane [Cu(1)–O 1.956(4)–1.979(4) Å] and by an aqua ligand at the apical position [Cu(1)–O(1w) 2.202(5) Å; O(1w)–Cu(1)–O 89.2(2)–95.9(2)°] to form a square pyramid. Each terminal Cu^{II} is quadruply connected to Gd^{III} via four *syn, syn*-acetato-*O, O'* bridges with a Cu^{II}...Gd^{III} distance of 3.561(1) Å. A pair of the Gd^{III} atoms in two centrosymmetrically related dinuclear Cu–Gd subunits are each linked to the central Cu(2) atom by a single *syn, anti*-carboxylato-*O, O'* group, resulting in a pentanuclear molecule. The Cu(2)...Gd(1) distance of 4.662(1) Å is much longer than the Cu(1)...Gd(1) distance. Besides the five carboxy oxygen atoms [Gd–O 2.325(5)–2.397(5) Å], the co-ordination sphere of each Gd^{III} is completed by three aqua ligands [Gd–O(w) 2.434(5)–2.452(4) Å] to form an eight-co-ordinate distorted square-antiprism. The Cu(2) atom, located at a crystallographic inversion centre, is co-ordinated by two oxygen atoms from bridging acetate groups and two from monodentate acetate groups in a slightly distorted square-planar fashion [O(51)–Cu(2)–O(61) 89.3(2)°, Cu(2)–O 1.959(4)–1.970(5) Å]. Noteworthy is the fact that the other four oxygen atoms of the carboxylate groups about the Cu(2) atom are in close contact with it [Cu(2)...O(52) and Cu(2)...O(62) 2.759(5) and 2.846(5) Å, respectively], indicative of some weak interaction.^{7f} The co-ordination environment of the Cu(2) atom is similar to that found for monomeric copper(II) tetracarboxylates.¹³

The structure of the dinuclear Cu^{II}–Gd^{III} subunits is very similar to those found for two Cu^{II}–Ca^{II} complexes^{7c,e} and a dinuclear Cu^{II}–La^{III} complex with pyridinioacetate,⁹ but different from that found for a dinuclear Cu^{II}–Ca^{II} complex linked by a triple carboxylato-*O, O'* bridge of trimethylammonioacetate.^{7f} It is noteworthy that no heterometallic complexes containing both transition and lanthanoid ions bridged *uniquely* by carboxylate groups has been reported in the literature. Moreover all the structurally and magnetically characterized heterometallic Cu^{II}–Ln^{III} complexes reported to date are bridged by either phenoxo ligands¹ or other multidentate ligands with hetero donating groups.² Thus complex **1** serves as the first example of a Cu^{II}–Ln^{III} complex bridged only by carboxylate groups and is a new model complex for magnetic investigation. Further study on the synthesis and magnetic properties of this and related complexes is in progress.

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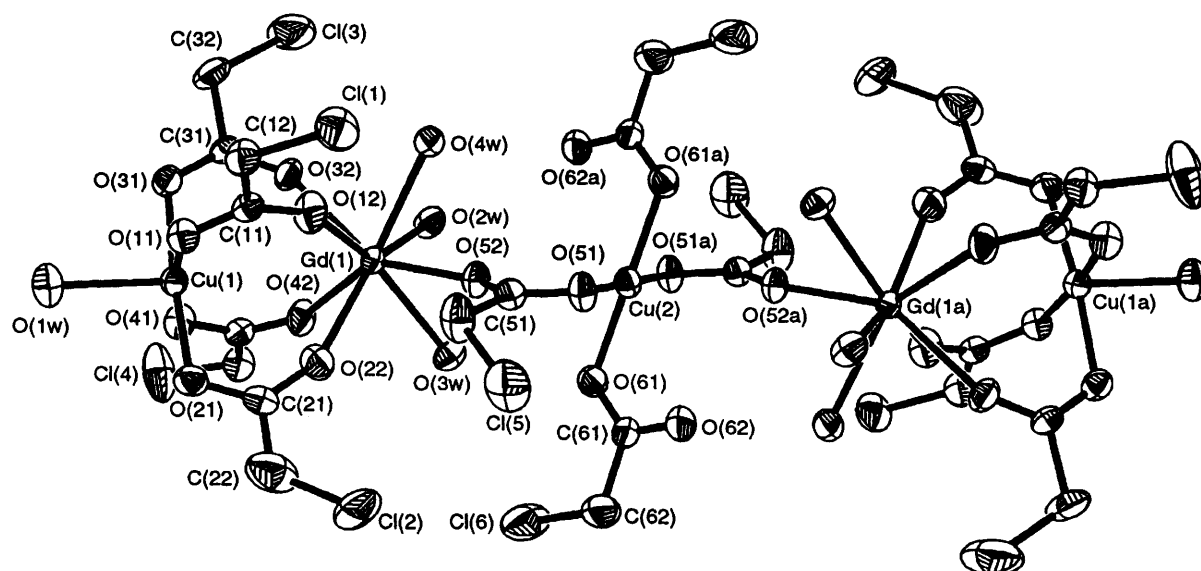


Fig. 1 ORTEP¹² drawing (at 35% probability level) of the pentanuclear molecule in **1**. Selected bond lengths (Å): Gd(1)–O(32) 2.325(5), Gd(1)–O(52) 2.337(4), Gd(1)–O(42) 2.352(5), Gd(1)–O(22) 2.379(5), Gd(1)–O(12) 2.397(5), Gd(1)–O(4w) 2.434(5), Gd(1)–O(3w) 2.441(4), Gd(1)–O(2w) 2.452(4), Cu(1)–O(31) 1.956(4), Cu(1)–O(21) 1.968(5), Cu(1)–O(41) 1.969(4), Cu(1)–O(11) 1.979(4), Cu(1)–O(1w) 2.202(5), Cu(2)–O(51) 1.959(4), Cu(2)–O(61) 1.970(5). Symmetry code: a 1 – x, y, 1 – z

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