DALTON
COMMUNICATION

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

Xiao-Ming Chen,* Ming-Liang Tong, Yu-Luan Wu and Yu-Ji Luo

Department of Chemistry, Zhongshan University, 135 Xingang Rd. W., Guangzhou 510275, China

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}_2–M^{II} (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 $Cu^{II}_{12}Ln^{III}_6$ (Ln = lanthanoid) clusters containing carboxylate bridges of zwitterionic pyridinioacetate and hydroxy bridges[8] 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 $[Cu_3Gd_2(O_2CCH_2Cl)_{12}(H_2O)_8]\cdot 2H_2O$ **1**.

Complex **1** was synthesized by the self-assembly of Cu^{II} and Gd^{III} ions with chloroacetate. An aqueous solution (2 cm^3) 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 $Cu(NO_3)_2\cdot 3H_2O$ (0.24 g, 1.0 mmol) was added with stirring at 60 °C for 10 min and followed with aqueous $Gd(NO_3)_3$ (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** consists of a centrosymmetrical pentanuclear $[Cu_3Gd_2(O_2CCH_2Cl)_{12}(H_2O)_8]$ 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 $Cu^{II}\cdots Gd^{III}$ 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 ligands[1] 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.

Acknowledgements

This work was supported by Guangdong Natural Science Foundation and Zhongshan University.

References

1 M. Andruh, I. Ramade, E. Codjovi, O. Giullou, O. Kahn and J. C. Trombe, *J. Am. Chem. Soc.*, 1993, **115**, 1822; M. Andruh, O. Kahn, J. Sainto, Y. Dromzee and S. Jeannin, *Inorg. Chem.*, 1993, **32**, 1623.

---

† Found: C, 15.90; H, 2.25. Calc. for $C_{24}H_{44}Cl_{12}Cu_3Gd_2O_{34}$ **1**: C, 16.00; H, 2.45%. IR data ($\tilde{\nu}/cm^{-1}$): 3367s (br), 3015w, 2959w, 1672vs, 1616vs, 1405vs (br), 1257s, 1145w, 1117w, 1089w, 934w, 793m, 716m, 688m, 625w and 582w.

‡ Crystal data for complex **1**: $C_{24}H_{44}Cl_{12}Cu_3Gd_2O_{34}$, M_r = 1807.11, monoclinic, space group $P2_1/c$, a = 10.521(2), b = 18.024(4), c = 15.310(3) Å, β = 99.85(3)°, U = 2860.4(10) $Å^3$, 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 ($2 \leq \theta \leq 26.5°$) 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 $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}} = 0.1804$ for 358 parameters and all 6194 unique reflections and conventional $R1 = 0.0551$ with the weighting scheme $w = 1/[\sigma^2(F_o) + (0.1000P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$; 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.

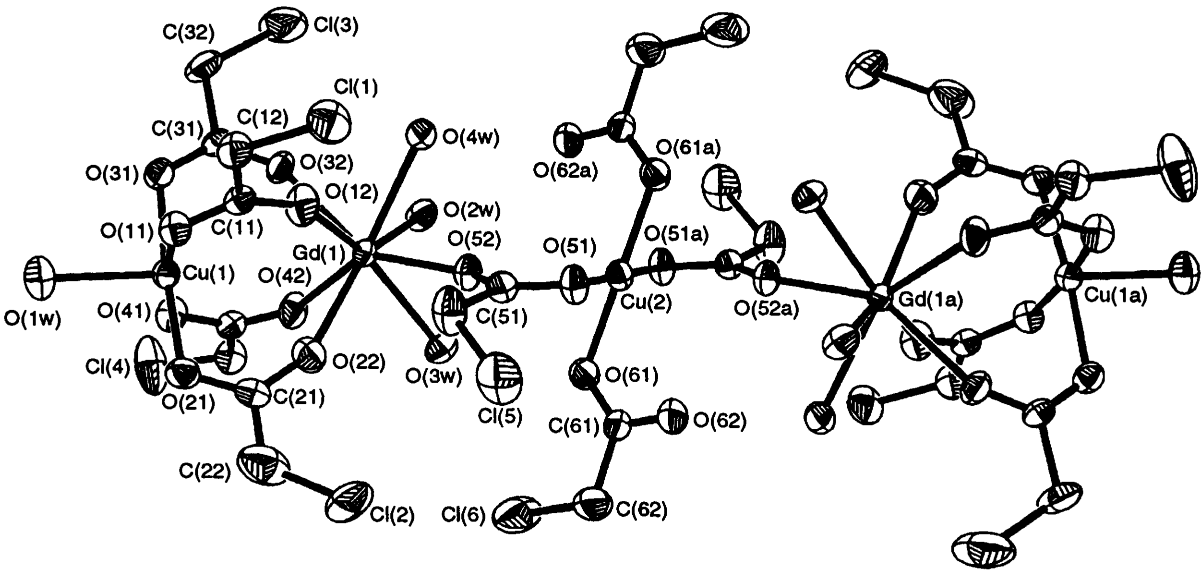

Fig. 1 ORTEP[12] drawing (at 35% probability level) of the pentanuclear molecule in **1**. Selected bond lengths (Å): Gd(1)–O(32) 2.325(5), Gd(1)–O(52) 2.337(4), Gd(1)–O(42) 2.352(5), Gd(1)–O(22) 2.379(5), Gd(1)–O(12) 2.397(5), Gd(1)–O(4w) 2.434(5), Gd(1)–O(3w) 2.441(4), Gd(1)–O(2w) 2.452(4), Cu(1)–O(31) 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 $1 - x, y, 1 - z$

2 O. Giullou, O. Kahn, R. Oushoorn, K. Boubeker and P. Batail, *Inorg. Chim. Acta*, 1992, **189–200**, 1190; R. Georges, O. Kahn and O. Giullou, *Phys. Rev. B*, 1994, **49**, 3235; Y.-T. Li, Z.-H. Jiang, S.-L. Ma, X.-Y. Li, D.-Z. Liao, S.-P. Yan and G.-L. Wang, *Transition Met. Chem.*, 1994, **14**, 432.

3 S. Wang, Z. Pang and D. L. Smith, *Inorg. Chem.*, 1993, **32**, 4992; A. J. Blake, V. A. Cherepamov, A. A. Dunlop, C. M. Grant, P. E. Y. Milne, J. M. Rawson and R. E. Winpenny, *J. Chem. Soc., Dalton Trans.*, 1994, 2719; A. J. Blake, R. O. Gould, P. E. Y. Milne and R. E. Winpenny, *J. Chem. Soc., Chem. Commun.*, 1992, 522; D. M. L. Goodgame, D. J. Williams and R. E. Winpenny, *Polyhedron*, 1989, **8**, 1531, and refs. therein.

4 C. Mehrotra and R. C. Bohra, *Metal Carboxylates*, Academic Press, New York, 1983; A. Ouchi, Y. Suzuki, Y. Ohki and Y. Koizumi, *Coord. Chem. Rev.*, 1988, **92**, 29; F. A. Cotton and R. A. Walton, *Struct. Bonding (Berlin)*, 1985, **62**, 1; M. Melnik, *Coord. Chem. Rev.*, 1982, **42**, 259; R. D. Cannon and R. P. White, *Prog. Inorg. Chem.*, 1988, **36**, 195.

5 R. Holtzelmann, K. Wieghardt, J. Ensling, H. Romstedt, P. Gütlich, E. Bill, U. Flörke and H.-J. Haupt, *J. Am. Chem. Soc.*, 1992, **114**, 9470; A. S. Bovorik, M. P. Hendrich, T. R. Holman, E. Munck, V. Papaefthymiou and L. Que, jun., *J. Am. Chem. Soc.*, 1990, **112**, 6031; T. Tanase, S. P. Watton and S. J. Lippard, *J. Am. Chem. Soc.*, 1994, **116**, 9401, and refs. therein.

6 W. Clegg, I. R. Little and B. P. Straughan, *J. Chem. Soc., Dalton Trans.*, 1988, 1916; 1986, 1283.

7 (*a*) D. A. Langs and C. R. Hare, *Chem. Commun.*, 1967, 890; (*b*) M. B. Cingi, A. M. M. Landredi, A. Tiripicchio and M. Tiripicchio, *Acta Crystallogr., Sect. B*, 1977, **33**, 659; (*c*) G. Smith, E. J. O'Reilly, C. H. L. Kennard and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1985, 243; (*d*) M. J. Sanchis, P. Gomez-Romero, J.-V. Folgado, F. Sapina, R. Ibanez, A. Beltran, J. Garcia and D. Beltran, *Inorg. Chem.*, 1992, **31**, 2915; (*e*) X.-M. Chen and T. C. W. Mak, *Polyhedron*, 1994, **13**, 1087; (*f*) X.-M. Chen and T. C. W. Mak, *Inorg. Chem.*, 1994, **33**, 2444.

8 X.-M. Chen, S. J. M. Aubin, Y.-L. Wu, Y.-S. Yang, T. C. W. Mak and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1995, **116**, 9600.

9 X.-M. Chen and Y.-L. Wu, unpublished work.

10 G. M. Sheldrick, SHELXL 93, Program for X-Ray Crystal Structure Refinement, University of Göttingen, 1993.

11 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

12 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

13 X.-M. Chen and T. C. W. Mak, *Polyhedron*, 1992, **11**, 2567.

Received 2nd February 1996; *Communication* 6/00793G