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Synthesis and structure of an unprecedented heterometallic tetranuclear cluster $[Gd_2Co_2(\mu_4\text{-}O)(\mu\text{-}H_2O)(CDTA)_2(H_2O)_6]\cdot 10H_2O$ (H_4CDTA = *trans*-1,2-cyclohexanedinitrilotetraacetic acid)

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A novel tetranuclear lanthanide-transition metal cluster $[Gd_2Co_2(\mu_4\text{-}O)(\mu\text{-}H_2O)(CDTA)_2(H_2O)_6]\cdot 10H_2O$ has been synthesized, in which the cluster core is held together through $\mu_4\text{-}O^{2-}$, $\mu\text{-}H_2O$ and μ-carboxylate bridges.

Polynuclear complexes containing both 4f and 3d ions have attracted great interest in view of their magnetic and electronic properties.[1–10] The studies were mainly focused on the Gd–Cu pair, since the Gd, with an $^8S_{7/2}$ single-ion ground state, does not possess a first-order orbital moment and a ferromagnetic interaction is often present between Gd and Cu. In contrast, the investigations for other Ln–M systems are relatively rare.[11] Of course, the synthetic difficulties are a critical factor in restricting further study due to the large differences between the chemical properties of lanthanide and transition metals. Aminopolycarboxylic acids are demonstrated as a good choice for the assembly of 4f–3d complexes owing to their numerous coordination sites and flexible connection modes. Many fascinating structures have been synthesized based on EDTA,[12] DTPA (diethylenetriaminepentaacetic acid),[13] NTA (nitrilotriacetic acid), IDA (iminodiacetic acid).[14] Here, a novel tetranuclear cluster $[Gd_2Co_2(\mu_4\text{-}O)(\mu\text{-}H_2O)(CDTA)_2(H_2O)_6]\cdot 10H_2O$ **1** (H_4CDTA = *trans*-1,2-cyclohexanedinitrilotetraacetic acid) bridged by three different bridges, namely oxo, aqua, and carboxylate is reported.

Compound **1** was prepared by mixing H_4CDTA (3 mmol), $CoCO_3$ (3 mmol) and $Gd(OH)_3$ (2 mmol) in 50 ml aqueous solution under stirring and heating. When the suspension became clear, 0.1 M NaOH aqueous solution was added dropwise to adjust the pH value to 4.5 and the mixture was continually heated for 0.5 h. Then, the resulting solution was condensed and filtered. The filtrate was allowed to stand at room temperature. After three months, pink needle-like crystals were obtained.†

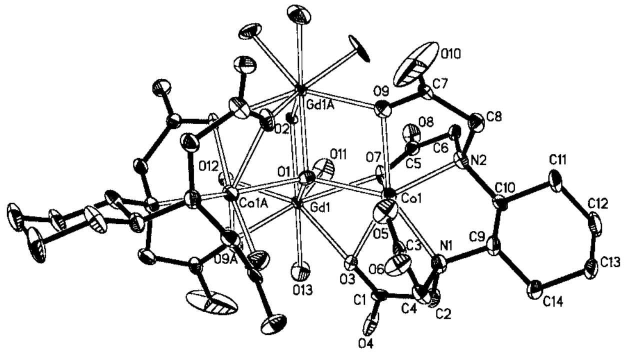


Fig. 1 The structure of complex **1** and selected bond lengths (Å) and angles (°): Co(1)–O(5) = 2.01(2), Co(1)–N(2) = 2.165(14), Co(1)–O(7) = 2.18(2), Co(1)–N(1) = 2.201(17), Co(1)–O(1) = 2.226(8), Co(1)–O(9) = 2.40(2), Co(1)–O(3) = 2.395(16), Gd(1)–O(9a) = 2.339(19), Gd(1)–O(1) = 2.346(13), Gd(1)–O(2) = 2.352(13), Gd(1)–O(12) = 2.386(16), Gd(1)–O(13) = 2.404(11), Gd(1)–O(3) = 2.421(18), Gd(1)–O(11) = 2.44(2), Gd(1)–O(7) = 2.456(9); Co(1)–O(1)–Co(1a) = 143.0(11), Co(1)–O(1)–Gd(1a) = 105.9(2), Co(1)–O(1)–Gd(1) = 95.4(2), Gd(1a)–O(1)–Gd(1) = 109.0(9), Gd(1)–O(2)–Gd(1a) = 108.5(9). Symmetry code a: $-x + 1, y, -z + 2$.

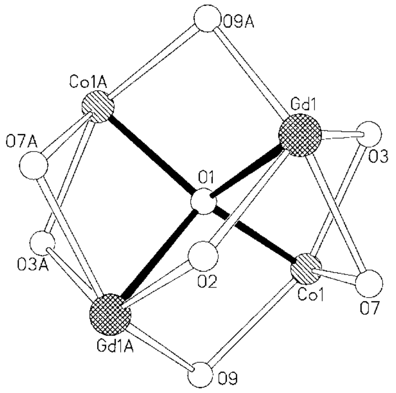
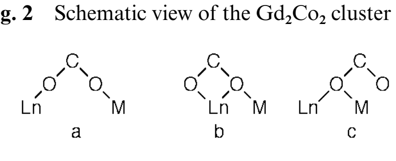


Fig. 2 Schematic view of the Gd_2Co_2 cluster core.



Scheme 1

X-Ray analysis revealed that **1** consists of a tetranuclear Gd_2Co_2 cluster bridged by $\mu_4\text{-}O^{2-}$, $\mu\text{-}H_2O$ and carboxylate as illustrated in Fig. 1.‡ Two pairs of crystallographically-related Gd and Co ions are connected through a central oxo sitting on a C_2 axis to give rise to a tetrahedral structure with Gd1–O1 and Co1–O1 bond lengths being 2.346(13) and 2.226(8) Å, respectively. Meanwhile, the two Gd(III) ions are also bridged by one aqua ligand (O2) lying on a C_2 axis with Gd1–O2 distance 2.352(13) Å, which is in the range for the coordinated aqua ligands.[15] The adjacent Gd and Co ions are linked by two different types of connection mode. Gd1 and Co1 are connected by two carboxyl groups, see Scheme 1 mode c [Gd1–O3 = 2.421(18), Gd1–O7 = 2.456(9), Co1–O7 = 2.18(2), Co1–O3 = 2.395(16) Å], in addition to the central oxo group. Whereas Gd1a and Co1 are only bridged by one carboxyl group in the same mode as Gd1 [Gd1a–O9 = 2.339(19), Co1–O9 = 2.40(2) Å]. Thus, the Gd_2Co_2O tetrahedral core is further stabilized by these bridging groups as depicted in Fig. 2. It is noteworthy that the bridging mode of μ-O for the carboxylate is the first observed for 4f–3d complexes. In most cases, the carboxyl groups serve as a bridge as shown in Scheme 1a and 1b.[12,16] For lanthanide complexes, connection mode **1c** is less common.[17] Each Gd ion is eight coordinated by one central oxo, one bridging aqua ligand, three carboxyl atoms, and three terminal water molecules, forming a distorted square antiprism coordination

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environment, in which the top and bottom planes are occupied by O7, O11, O3, O13 and O2, O1, O12, O9a, respectively, with a dihedral angle of 8.9°. The Co(II) ion completes its coordination sphere by one central oxo [Co1–O1 = 2.226(8) Å], two nitrogen atoms [Co1–N1 = 2.201(17), Co1–N2 = 2.165(14) Å], three bridging carboxyl oxygen atoms [Co1–O7 = 2.18(2), *Co1–O9* = 2.40(2), Co1–O3 = 2.395(16) Å] and one terminal carboxyl atom [Co1–O5 = 2.01(2) Å], leading to a monocapped trigonal prism, in which the central oxo takes up the side face position. The neighboring Gd···Gd and Co···Co separations are 3.8180(11) and 4.2217(54) Å, respectively. The distance between Gd···Co connected through double carboxyl bridges is 3.3826(29) Å, shorter than that bridged by one carboxyl group [3.6505(30) Å]. It is noted that the Ln···M separations connected by the single atom carboxylate bridges (Scheme 1c) are the shortest among the three bridging modes, for example, in $Ln_2M_3(EDTA)(H_2O)_{11}\cdot 12H_2O$[12] (Scheme 1b, 4.8–4.9 Å) and in $\{[GdMn(H_2O)_5(DTPA)]\cdot H_2O\}_\infty$ (Scheme 1a, 5.6 Å).[13] The shorter distance may favor the magnetic coupling.

In compound **1**, the transition metal Co ion is chelated by the CDTA ligand and the Gd ion is hydrated, similar to that observed in 2-D $Ln_2M_3(EDTA)(H_2O)_{11}\cdot 12H_2O$, but different from the $\{[GdMn(H_2O)_5(DTPA)]\cdot H_2O\}_\infty$ complex in which Gd and Mn ions are surrounded by the DTPA and aqua ligands, respectively.

Reported Ln_2M_2 cluster cores are relatively rare. The known $[Dy(hfac)_3Cu(Satn)(OH)]_2$ (hfac = hexafluoroacetylacetone, Satn = *N*-(3-aminopropyl)salicylaldiminato) exhibits a stepped geometry,[18] in which two μ_3-OH groups link the Dy and Cu. In the other three complexes, $Cu_2Gd_2(mhp)_4(OMe)_2(NO_3)_4(Hmhp)_2(MeOH)_2$, $[Co_2Dy_2(OH)(chp)_6(NO_3)_5]^{2+}$ and $Cu_2La_2(chp)_8(Hchp)_2(NO_3)_2]\cdot 2(Hchp)\cdot 2MeCN$,[19] the four metals are arranged in a butterfly fashion (Hmhp = 6-methyl-2-hydroxypyridine, chp = 6-chloro-2-pyridonate). Another case is $[Fe_2(CN)_4(phen)_4Yb_2Cl_6(H_2O)_2]\cdot 2H_2O\cdot 2CH_3OH$ (phen = 1,10-phenanthroline) in which Fe and Yb ions are connected through cyanide to produce a rhombus structure.[20]

Compound **1** is remarkably different from those mentioned above. It has a unique feature that two Gd and two Co ions are held together *via* a μ_4-O^{2-}, leading to a tetrahedron motif. To the best of our knowledge, it serves as the first case of Ln–M complexes bridged by μ_4-O^{2-}. In addition, it is somewhat unusual to find μ_4-O^{2-}, μ-H_2O and μ-carboxylate bridges simultaneously within the same structure. Moreover, the single μ-O of carboxylate firstly observed in this case supplies a new magnetic coupling mode for the 4f–3d heterometallic compounds and might be expected to show interesting magnetic interactions due to shorter metal–metal separations. Further investigation on the magnetic properties of this compound is in progress.

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Notes and references

† Elemental analysis for compound **1**: Calc. for $C_{28}H_{70}Co_2Gd_2N_4O_{34}$: C, 23.35; H, 4.86; N, 3.89. Found: C, 23.79; H, 4.70; N, 3.97%. UV-Vis spectrum of the pink aqueous solution for compound **1** shows a band at 539 nm, indicative of a +2 oxidation state for the cobalt ions.[21]

‡ Crystal data: $C_{28}H_{70}Co_2Gd_2N_4O_{34}$, $M = 1439.24$, monoclinic, $C2$, $a = 24.940(2)$, $b = 9.7718(8)$, $c = 10.1941(6)$ Å, $\beta = 109.640(5)°$, $U = 2339.9(3)$ Å^3, $Z = 2$, $D_c = 2.043$ Mg m^{-3}, $\mu = 3.604$ mm^{-1}, $F(000) = 1440$, GoF = 1.173. The final R_1 and wR_2 are 0.0712 and 0.1821 for 301 parameters and 3777 reflections $[I > 2\sigma(I)]$. CCDC reference number 186/1861. See http://www.rsc.org/suppdata/dt/b0/b000490l/ for crystallographic files in .cif format.

1 A. Bencini, C. Benelli, A. Caneschi, R. L. Carlin, A. Dei and D. Gatteschi, *J. Am. Chem. Soc.*, 1985, **107**, 8128; C. Benelli, A. Caneschi, D. Gatteschi, O. Guillou and L. Pardi, *Inorg. Chem.*, 1990, **29**, 1751.

2 I. Ramade, O. Kahn, Y. Teannin and F. Robert, *Inorg. Chem.*, 1997, **36**, 930; M. Andruh, I. Ramade, E. Codjovi, O. Guillou, O. Kahn and J. Trombe, *J. Am. Chem. Soc.*, 1993, **115**, 1822.

3 S. Decurtins, M. Gross, H. W. Schmalle and S. Ferlay, *Inorg. Chem.*, 1998, **37**, 2443.

4 X. M. Chen, M. L. Tong, Y. L. Wu and Y. J. Luo, *J. Chem. Soc., Dalton Trans.*, 1996, 2181.

5 J.-P. Costes, F. Dahan, A. Dupuis and J.-P. Laurent, *Inorg. Chem.*, 1996, **35**, 2400; J.-P. Costes, F. Dahan, A. Dupuis and J.-P. Laurent, *Chem. Eur. J.*, 1998, **4**, 1616; J.-P. Costes, A. Dupuis and J.-P. Laurent, *Eur. J. Inorg. Chem.*, 1998, 1543.

6 S. Wang, Z. Pang, K. D. L. Smith, Y. S. Hua, C. Deslippe and M. J. Wagner, *Inorg. Chem.*, 1995, **34**, 908; S. Wang, Z. Pang and K. D. L. Smith, *Inorg. Chem.*, 1993, **32**, 4992.

7 J. G. Mao, L. Song, X. Y. Huang and J. S. Huang, *Polyhedron*, 1997, **16**, 963.

8 N. Sakagami and K. Okamoto, *Chem. Lett.*, 1998, 201; N. Sakagami, M. Tsunekawa, T. Konno and K. Okamoto, *Chem. Lett.*, 1997, 575.

9 T. Sanada, T. Suzuki, T. Yoshida and S. Kaizaki, *Inorg. Chem.*, 1998, **37**, 4712 and references therein.

10 A. J. Blake, R. O. Gould, C. M. Grant, P. E. Y. Milne, S. Parsons and R. E. P. Winpenny, *J. Chem. Soc., Dalton Trans.*, 1997, 485; S. J. Archibald, A. J. Blake, S. Parsons, M. Schroder and R. E. P. Winpenny, *J. Chem. Soc., Dalton Trans.*, 1997, 173.

11 C. Piguet, E. Rivara-Minten, G. Bernardinelli, J.-C. G. Bunzli and G. Hopfgartner, *J. Chem. Soc., Dalton Trans.*, 1997, 421; J.-P. Costes, F. Dahan, A. Dupuis and J.-P. Laurent, *Inorg. Chem.*, 1997, **36**, 4284; J. Lisowski and P. Starynowicz, *Inorg. Chem.*, 1999, **38**, 1351.

12 T. Yi, S. Gao and B. G. Li, *Polyhedron*, 1998, **17**, 2243.

13 T. Z. Jin, S. F. Zhao, G. X. Xu, Y. Z. Han, N. C. Shi and Z. S. Ma, *Acta Chim. Sin.* (*Chin. Ed.*), 1991, **49**, 569; W. C. Yang, J. R. Li, Y. F. Zhou and T. Z. Jin, *Acta Chim. Sin.* (*Chin. Ed.*), 1996, **54**, 795.

14 Q. D. Liu, S. Gao, J. R. Li, Q. Z. Zhou, K. B. Yu, B. Q. Ma, S. W. Zhang, X. X. Zhang and T. Z. Jin, submitted for publication.

15 J.-P. Costes, F. Dahan and A. Dupuis, *Inorg. Chem.*, 2000, **39**, 165.

16 M. Andruh, I. Ramade, E. Codjovi, O. Guillou, O. Kahn and J. C. Trombe, *J. Am. Chem. Soc.*, 1993, **115**, 1822; Y. Y. Yang, Y. L. Wu, L. S. Long and X. M. Chen, *J. Chem. Soc., Dalton Trans.*, 1999, 2005.

17 J. F. Ma and J. Z. Ni, *Prog. Chem.* (*Chinese*), 1996, **8**, 259; H. P. Bommeli, G. Anderegg and W. Petter, *Z. Kristallogr.*, 1986, **174**, 23.

18 C. Benelli, A. Caneschi, D. Gatteschi, O. Guillou and L. Pardi, *Inorg. Chem.*, 1990, **29**, 1750.

19 C. Benelli, A. J. Blake, P. E. Y. Milne, J. M. Rawson and R. E. P. Winpenny, *Chem. Eur. J.*, 1995, 614; A. J. Blake, P. E. Y. Milne and R. E. P. Winpenny, *J. Chem. Soc., Dalton Trans.*, 1993, 3727; E. K. Brechin, S. G. Harris, S. Parsons and R. E. P. Winpenny, *J. Chem. Soc., Dalton Trans.*, 1997, 1665.

20 K. Harada, J. Yuzurihara, Y. Ishii, N. Sato, H. Kambayashi and Y. Fukuda, *Chem. Lett.*, 1995, 887.

21 A. P. B. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, 1986.

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