Synthesis and Structure of Novel Oxalate-Bridged Hexanuclear Lanthanide(III)-Chromium(III) Complexes

Xing Zhang, Yong Cui, Fakun Zheng, and Jinshun Huang*
State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter,
Chinese Academy of Science, Fuzhou, Fujian 350002, P.R. China

(Received June 28, 1999; CL-990577)

Hexanuclear lanthanide(III)-chromium(III) complexes $[Ln_2(\mu\text{-ox})\{Cr(bipy)(\mu\text{-ox})(ox)\}_4(H_2O)_6]\cdot 13H_2O$ (Ln = Pr **1**, Gd **2**) (bipy = 2,2' -bipyridine and ox = oxalate dianion) have been synthesized by reaction of $[Cr(bipy)(ox)_2]^-$ building blocks with Ln(III) ions. The structure of **1** has been determined by X-ray crystallography.

The synthesis and characterization of heteropolynuclear complexes comprising simultaneously lanthanide and transition metal ions have received much interest in view of the peculiar magnetic, electronic and spectroscopic properties arising from metal–metal interactions.[1-8] This interest has been essentially focused on the Gd(III)-Cu(II) couple which has been found to be directly ferromagnetic irrespective of the details of nuclearity and nature of the bridging ligands.[1-5] Recent studies have further demonstrated that the magnitude of the ferromagnetic exchange interaction between the different metal centres is exponentially dependent on the Gd-Cu distance.[4] By comparison, the chemistry of other 3d-4f mixtures have been poorly investigated, and in fact only very few structurally characterized complexes are known which contain such combinations of metals.[6-8] We have recently synthesized and structurally characterized several Ln-Co and Ln-Zn mixed-metal compounds bridged by carboxylate ligands.[8] We now report the reaction of $[Cr(bipy)(ox)_2]^-$ building blocks with Ln(III) ions to produce the novel heterohexanuclear compounds $[Ln_2(\mu\text{-ox})\{Cr(bipy)(\mu\text{-ox})(ox)\}_4(H_2O)_6]\cdot 13H_2O$ (Ln = Pr **1**, Gd **2**).

An aqueous solution (60 ml) containing $LnCl_3\cdot 6H_2O$ (Ln = Pr **1**, Gd **2**) (1mmol) and $[NaCr(bipy)(ox)_2H_2O]\cdot 2H_2O$ (1.38g, 3mmol), prepared according to the literature method,[9] was stirred for a few minutes and then filtered. The filtrate was kept at room temperature for several days to give red crystals. Satisfactory element analyses were obtained for both complexes.[10] The IR spectra of them are similar and each displays two strong bands at 1722 and 1651 cm^{-1} attributable to the $\nu_{as}(COO^-)$, and two strong bands at 1448 and 1375 cm^{-1} due to the $\nu_s(COO^-)$, indicative of the presence of two different geometries of the oxalate ligands, and characteristic absorptions corresponding to bipy groups (806, 771, 731 cm^{-1}). The structure of complex **1** has been determined by single crystal X-ray crystallography,[11] while cell determination suggests that complex **2** is isostructural to **1**.[12]

The molecular structure of **1** is shown in Figure 1. This complex consists of discrete centrosymmetric hexanuclear $\{Pr_2Cr_4\}$ units containing four $[Cr(bipy)(ox)_2]^-$ anions, one oxalate anion and two Pr^{3+} ions, the inversion residing on the midpoint of the vector of Pr-PrA. A pair of Pr^{3+} ions in two centrosymmetrically related trinuclear $\{PrCr_2\}$ subunits are linked together by an oxalate bridge with the Pr···PrA distance of 6.427(2) Å. Besides this bridging oxalate anion, the nine coordination geometry of Pr center is further completed by four carboxyl oxygen atoms from two oxalate groups of two $[Cr(bipy)(ox)_2]^-$ units and three water molecules, with the Pr-O bond lengths ranging from 2.440(6) to 2.603(7) Å. The geometry of the Pr center can be best described as a distorted monocapped square antiprism: one square face consists of atoms O(1), O(3), O(51) and O(22), whereas another face is defined by O(2), O(12), O(11) and O(21). The dihedral angle between the two square planes is 5.05°. Four $[Cr(bipy)(ox)_2]^-$ units show almost the same structure, and each chromium atom is six–coordinated in a distorted octahedral coordination with two bipy nitrogen atoms from one bidentate bipy and four oxygen atoms from two oxalate groups. There are two types of oxalate groups in each $[Cr(bipy)(ox)_2]^-$ unit: bridging and terminal. The Cr–O bond distances for the terminal oxalate ligand (av. 1.940(6) Å) are shorter than those for the bridging oxalate ligand (av. 1.982(6) Å). The Cr–N(bipy) bond lengths (av. 2.039(8) Å) are within the range observed for the general bipy–containing chromium complexes.[9,13] The average distance between the adjacent Pr and Cr metals is 5.803(2) Å, which is shorter than the Ce···Cr distance of $[CrCe(ox)_3(H_2O)_4]_2\cdot 12H_2O$ (5.93 Å) and the Nd···Cr distance of $[Nd\{Cr(eddp)(ox)\}_3(H_2O)_3]\cdot 12H_2O$ (5.876(2) Å)

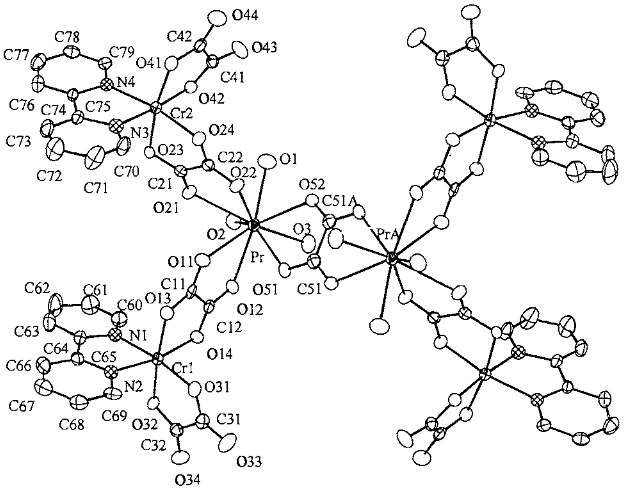

Figure 1. Molecular structure of complex **1**. Hydrogen atoms are omitted for clarity. Selected bond distances (Å): Pr-O(1) 2.470(7), Pr-O(2) 2.523(6), Pr-O(3) 2.478(7), Pr-O(11) 2.603(7), Pr-O(12) 2.495(6), Pr-O(21) 2.569(6), Pr-O(22) 2.556(6), Pr-O(51) 2.440(6), Pr-O(52) 2.504(6), Cr(1)-O(13) 1.976(6), Cr(1)-O(14) 1.986(6), Cr(1)-O(31) 1.945(6), Cr(1)-O(32) 1.934(6), Cr(2)-O(23) 1.986(6), Cr(2)-O(24) 1.979(6), Cr(2)-O(41) 1.931(6), Cr(2)-O(42) 1.951(6), Cr(1)-N(1) 2.041(7), Cr(1)-N(2) 2.045(8), Cr(2)-N(3) 2.033(8), Cr(2)-N(4) 2.038(7). Symmetry code: A 1-x, -y, -z.

(eddp = ethylenediamine–N,N'–dipropionate), but longer than the Yb$\cdots$Cr distance of [$(acac)_2Cr(ox)Yb(HBpz_3)_2$] (5.631(1) Å) (acac = acetylacetonate, $HBpz_3$ =hydrotris(pyrazol–1–yl)borate).[6] This suggests the possibility of magnetic exchange interaction between Pr(III) and Cr(III) ions in this complex. Hydrogen bonding plays an important role in consolidating the crystal structure. The hexanuclear {Pr_2Cr_4} units are held together to form an extended layer structure by the intermolecular hydrogen bonds between the aqua ligands bonded to the Pr atoms and the terminal oxalate oxygen atoms with a distance O(2)$\cdots$O(44') = 2.732 Å (Symmetry code: ' x, 1/2-y, 1/2+z .).

Tris(oxalato)chromate(III), $[Cr(ox)_3]^{3-}$, and its derivatives such as $[Cr(bipy)(ox)_2]^-$ and $[Cr(salen)(ox)]^-$ (salen = N,N'-ethylenebis(salicylideneaminate)) are well known for their strong coordination ability to metal ions, allowing to preparation of a number of oxalate-bridged polynuclear assemblies.[6,13-15] The structure of the dinuclear [Pr{$Cr(bipy)(ox)_2$}] subunits in **1** is very similar to those found for the isolate and polymeric {M(II)-Cr_2} (M = Co, Cu, Mn, Ba) compounds with $[Cr(bipy)(ox)_2]^-$ units,[13] but the overall structure of complex **1** is not resemble to any structures reported for homo- and heteropolynuclear chromium and other metal oxalate complexes,[6,9,13-16] as well as other 3d-4f species reported previously. Much more interest is the presence of an oxalate anion between two Ln(III) ions, which clearly originated from the precursors $[Cr(bipy)(ox)_2]^-$, in contrast with the relative inertness of chromium(III) complexes.[6,13-15] Therefore, complex **1** is unique among chromium oxalate complexes and constitutes a new structural variety in metal carboxylate chemistry. Moreover complex **1**, to our knowledge, is the largest discrete oxalate-bridged Cr-containing heterometallic compounds that have been documented so far.

Further study on the synthesis and magnetic properties of a series of oxalate–bridged Ln(III)–Cr(III) complexes is in progress.

The research was supported by the National Science Foundation of China and Science Foundation of Fujian Province.

References and Notes

1 a) C. Benelli, A. Caneschi, D. Gatteschi, O. Guillou, and L. Pardi, *Inorg. Chem.*, **29**, 1751 (1990); b) N. Matsumoto, M. Sakamoto, H. Tamaki, H.Okawa, and S. Kida, *Chem. Lett.*, **1989**, 853.

2 a) 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; b) S. Wang, S. J. Trepanier, and M. J. Wagner, *Inorg. Chem.*, **32**, 833 (1993).

3 X. -M. Chen, Y. -L. Wu, Y. -X. Tong, and X. -Y. Huang, *J. Chem. Soc., Dalton Trans.*, **1996**, 2443.

4 a) M. Andruh, I. Ramade, E. Codjovi, O. Guillou, O. Kahn, Y. Jeannin, and F. Robert, *Inorg. Chem.*, **36**, 930 (1997) b) J. L. Sanz, R. Ruiz, A. Gleizes, F. Lloret, J. Faus, M. Julve, J. J. Borrás-Almenar, and Y. Journaux, *Inorg. Chem.*, **35**, 7384 (1996); c) C. Benelli, A. J. Blake, P. E. Y. Milne, J. M. Rawson, and R. E. P. Winpenny, *Chem. Eur. J.*, **1**, 614 (1995).

5 M. Andruh, I. Ramade, E. Codjovi, O. Guillou, O. Kahn, and J. C. Trombe, *J. Am. Chem. Soc.*, **115**, 1822 (1993).

6 a) S. Decurtins, M. Gross, H. W. Schmalle, and S. Ferlay, *Inorg. Chem.*, **37**, 2443 (1998); b) N. Sakagami, and K. Okamoto, *Chem. Lett.*, **1998**, 201; c) T. Sanada, T. Suzuki, T. Yoshida, and S. Kaizaki, *Inorg. Chem.*, **37**, 4712 (1998).

7 a) Y. Yukawa, S. Igarashi, A. Yamano, and S. Sato, *Chem. Commun.*, **1997**, 711; b) C. Piguet, J. -C. G. Büzli, G. Bernardinelli, G. Hopfgartne, S. Petoud, and O. Schaad, *J. Am. Chem. Soc.*, **118**, 6681 (1996); c) E. K. Brechin, S. G. Harris, S. Parsons, and R. E. P. Winpenny, *J. Chem. Soc., Dalton Trans.*, **1997**, 1665; d) J. -P. Costes, F. Dahan, A. Dupuis, and J. -P. Laurent, *Inorg. Chem.*, **36**, 3429 (1997); e) T. Sanada, T. Suzuki, and S. Kaizaki, *J. Chem. Soc., Dalton Trans.*, **1998**, 959.

8 a) Y. Cui, J. –T. Chen, D. -L. Long, F. -K Zheng, W. -D. Cheng, and J. –S. Huang, *J. Chem. Soc., Dalton Trans.*, **1998**, 2955; b) Y. Cui, F. -K. Zheng, and J. -S. Huang., *Chem. Lett.*, **1999**, 281.

9 M. C. Muñoz, M. Julve, F. Lloret, J. Faus, and M. Andruh, *J. Chem. Soc., Dalton Trans.*, **1998**, 3125.

10 Elemental analyses: **1**. Found: C, 32.58; H, 2.46; N, 5.30%. Calcd for $C_{58}H_{70}Cr_4N_8Pr_2O_{55}$: C, 30.98; H, 3.14; N, 4.98%. **2**. Found: C, 32.42; H, 2.75; N, 5.27%. Calcd for $C_{58}H_{70}Cr_4N_8Gd_2O_{55}$: C, 30.72; H, 3.09; N, 4.95%.

11 Crystal data for **1**: $C_{58}H_{70}Cr_4N_8Pr_2O_{55}$, F.W. = 2249.04, monoclinic, $P2_1/c$ (#14), a = 10.677(2), b = 17.770(4), c = 22.164(4) Å, β = 90.54(3)°, V = 4204.9(15) Å^3, Z = 2, D_c = 1.776 g·cm^{-3}, μ(Mo-Kα) = 1.749 mm^{-1}. Measurements were carried out on a Enraf-Nonius CAD4 diffractometer. The structure was solved by direct methods and refined by full-matrix least squares (on F^2). The final R_1 = 0.068 and wR = 0.161 for 5149 observed reflections ($I > 2.00\sigma(I)$).

12 Cell parameters for **2**: monoclinic, a = 10.686(2), b = 17.665(4), c = 22.140(4) Å, β = 90.63(3)°, V = 4178.7(14) Å^3.

13 a) S. Decurtins, H. W. Schmalle, R. Pellaux, P. Schneuwly, and A. Hauser, *Inorg. Chem.*, **35**, 1451 (1996); b) F. D. Rochon, R. Melanson, and M. Andruh, *Inorg. Chem.*, **35**, 6086 (1996); c) M. Andruh, R. Melansan, C. V. Stager, and F. D. Rochon, *Inorg. Chim. Acta.*, **251**, 309 (1996).

14 M. Ohba, H. Tamaki, N. Matsumoto, and H. Okawa, *Inorg. Chem.*, **32**, 5385 (1993).

15 a) H. Tamaki, Z. J. Zhong, N. Matsumoto, S. Kida, M. Koikawa, N. Achiwa, Y. Hashimoto, and H. Okawa, *J. Am. Chem. Soc.*, **114**, 6974 (1992); b) R. Pellaux, H. W. Schmalle, R. Huber, P. Fischer, T. Hauss, B. Ouladdiaf, and S. Decurtins, *Inorg. Chem.*, **36**, 2301 (1997).

16 a) S. Kitagawa, T. Okubo, S. Kawata, M. Kondo, M. Katada, and H. Kobayashi, *Inorg. Chem.*, **34**, 4790 (1995); b) M. Hernández-Molina, F. Lloret, C. Ruiz-Pérez, and M. Julve, *Inorg. Chem.*, **37**, 4131 (1998).