ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2009, Vol. 35, No. 2, pp. 157–159. © Pleiades Publishing, Ltd., 2009.

Formation of Oxalate Induced by 4,4'-Bipyridine: Hydrothermal Sheses of Two Erbium Coordination Polymers

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Received April 09, 2008

Abstract—Two different erbium(III) 5-nitroisophthalate coordination polymers were prepared based on the adjustement of 4,4'-Bipyridine. Structural analysis indicated that the production of the bridging oxalate group ($C_2O_4^{2-}$) may be attributed to the reductive coupling of CO_2 molecules from the decarboxylation of the 5-Nip^{2-} ligand (5-Nip^{2-}—anion of 5-nitroisophthalic acid), which is induced by 4,4'-Bipyridine.

DOI: 10.1134/S1070328409020122

INTRODUCTION

In the synthesis of carbon-containing compounds, carbon dioxide is a noticeable material because of its excessive existence in nature [1]. It is so easyly for the reductive coupling of carbon dioxide to oxalate in electrochemical methods [2], but a few of cases about metal complexes effecting CO_2 to $C_2O_4^{2-}$ have been reported. In these cases, some reactions were induced by low-valent metal ions as reductant, such as $Cp_2Ti^{III}(CH_2)NRCH_2CH_2NR(CH_2)_3Ti^{III}Cp_2$ (Cp = cyclopentadiene) [3], $(Me_5Cp)_2Sm(THF)_2$ [4] and [LCu(μ-C_2O_4)CuL][PhB]$_2$ (L = *N*,*N*,*N*'- triallyl–1.4,7–triazacyclononane) [5], while others reducing agents were vague mainly existing in lanthanide complexes [6]. This draws our attention to explore the mechanism of the formation of oxalate from reductive coupling of CO_2 in lanthanide complexes. We designed and obtained an erbium oxalate coordination polymer [Er(5-Nip)(C_2O_4)$_{0.5}$(H_2O)$_3$] · 2H_2O (**I**) without oxalate in reagents from the reaction of hydrated erbium nitrate, 5-nitroisophthalic acid (**5-H_2Nip**), and 4,4'-Bipyridine (**4,4'-Bipy**) under hydrothermal conditions. In the absence of Bipy, we gained another erbium complex without $C_2O_4^{2-}$ [Er(5-Nip)(5-HNip)(H_2O)$_2$] · 2H_2O (**II**).

EXPERIMENTAL

All the reagents used were of analytical grade and used without further purification.

Synthesis and X-ray diffraction analysis. Complex I was prepared with the ratio of ($Er(NO_3)_3$ · 6H_2O : 5-H_2Nip : 4,4'-Bipy : NaOH) = 1 : 1 : 1 : 2 under hydrothermal conditions at 155°C for 72 h. Some pink crystals are obtained for investigation (the yield is 15% based on erbium nitrate). Crystal data for **I**: pink sheet crystal, 0.31 × 0.25 × 0.08 mm; triclinic, space group $P\bar{1}$, a = 7.4104(7), b = 9.2049(8), c = 11.5236(1) Å, α = 74.100(1)°, β = 71.854(1)°, γ = 79.970(1)°, Z = 2, ρ_{calcd} = 2.371 mg m^{-3}. Of 3487 measured reflections, 2450 independent reflections with $I > 2\sigma(I)$ were used in reflections; $R_1(F)$ = 0.0200, $wR_2(F^2)$ = 0.0509 for all data; max/min residual electron density 0.718/–0.819 e Å^{-3}. Crystal data for II: pink prismatic crystal, 0.18 × 0.15 × 0.09 mm. Triclinic, space group $P\bar{1}$, a = 9.6437(8), b = 10.4200(8), c = 13.5737(1) Å, α = 112.246(1)°, β = 91.428(1)°, γ = 115.032(1)°, Z = 2, ρ_{calcd} = 1.960 mg m^{-3}. Of 7133 measured reflections, 5154 independent reflections with $I > 2\sigma(I)$ were used in reflections; $R_1(F)$ = 0.0269, $wR_2(F^2)$ = 0.0606 for all data; max/min residual electron density 0.711/–0.611 e Å^{-3}. The structures were all resolved by direct method and refined with full-matrix least-squares refinements based on F^2 using the SHELXTL program package [7–9].

Supplementary data have been deposited with the Cambridge Crystallographic Centre (CCDC no. 615945 and 294557). Copy of this information may be obtained free of charge (deposit@ccdc.cam.ac.uk or www:http:// www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

For complex **I**, the X-ray diffraction analysis reveals that the Er(III) atom lies in an eight-coordinated dodecahedron environment (Fig. 1), in which two oxygen atoms (O(1) and O(2)) come from a chelating car-

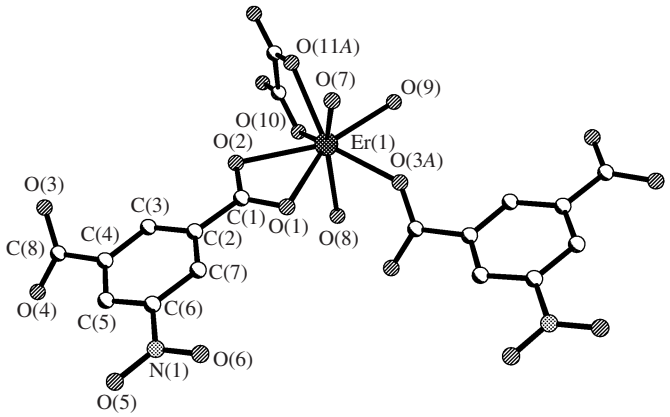

Fig. 1. Coordination environment of Er(III) in **I** (important bond lengths: Er(1)–O(8) 2.296(3); Er(1)–O(3)^{i} 2.304(3); Er(1)–O(7) 2.307(3); Er(1)–O(9) 2.322(3); Er(1)–O(11)^{ii} 2.352(3); Er(1)–O(10) 2.370(3); Er(1)–O(2) 2.403(3); Er(1)–O(1) 2.415(3) Å and angles: O(2)Er(1)O(1), 54.02(9)°; O(11)^{ii}Er(1)O(10) 68.70(9)° O(3)^{i}Er(1)O(9) 74.33(11)° (symmetry code: ^{i} $x, y + 1, z$; ^{ii} $-x, -y + 2, -z$).

boxyl group of the 5-Nip^{2-} ligand, one (O(3a)) from a monodentate carboxyl group of the 5-Nip^{2-} ligand, two (O(10) and O(11a)) from a chelate oxalate ligand, and the other three ones (O(7), O(8), and O(9)) are coordination water molecules. In **I**, two ligands coordinated to the erbium ion in two fashions, respectively: *bis*(chelate-monodentate) mode (Er···Er 9.205 Å) for 5-Nip^{2-} and *bis*(chelate) mode (Er···Er 6.131 Å) for the oxalate anion. The adjacent metal ions bridged by the oxalate anion as the parallel rings in z axis and by the 5-Nip^{2-} ligand as two long sides in y axis into a slightly slantwise 1D ladder (Fig. 2). The π–π packing interaction between the phenyls of the 5-Nip^{2-} ligands and hydrogen bonds in water joined the adjacent ladders into a porous three-dimensional supermolecular framework (Fig. 3).

Compound **I** has the same structure as the complexes $[Ln_2(5\text{-Nip})_2(C_2O_4)(H_2O)_6] \cdot (H_2O)_4$ (Ln = Eu, Gd) in [10] expecting that the oxalate anion (the yields are 65 and 57%) is from the reagents and that of **I**, probably, from reductive coupling of CO_2. We suppose that CO_2 generated by the decarboxylation of the 5-Nip^{2-} ligand couples into $C_2O_4^{2-}$. Probably, the low yield of **I** is indicative of the assumption. The decarboxylation reactions mostly occur under high-temperature conditions (160–270°C) [11]. Under hydro thermal reaction at 160°C, the mechanism of decarboxylation from carboxylate ligands to gain CO_2 is reasonable. In another case of terbium complexes with pyridinedicarboxylic acid (**H_2PDC**) [12], CO_2 species coming from the PDC^{2-} ligands was attributed to the C–C bond cleavage in the radical form. The decarboxylation and coupling reactions occurred in complexes mainly focus on lanthanide complexes, suggesting that the high oxophilicity or high coordination number of lanthanide ions play a significant role.

Instead of acting as a guest molecule in the complex reported, $\{[Er(5\text{-Nip})_2](4,4'\text{-}H_2Bipy)_{0.5}\}_n$ (the molar ratio of $Er(NO_3)_3 \cdot 6H_2O$: 5-H_2Nip : 4,4'-Bipy : NaOH = 2 : 2 : 1 : 4) [13], 4,4'-Bipy disappeared in the components of complex **I** with different stoichiometric ratios of reagents. This means that the increasing amount of 4,4'-Bipy benefits to the formation of the oxalate anion. In addtion, it is in the absence of 4,4'-Bipy that we obtained another new complex **II**, without any ingredient of oxalate anion, under the same experimental conditions (Fig. 4). This fact could indicate that an appropriate amount of 4,4'-Bipy accelerates or induces the decarboxylation of the 5-Nip^{2-}ligand and reductive coupling of CO_2 into $C_2O_4^{2-}$.

The TG–DTG analysis for complex **I** showed that its decomposition process is divided into four stages: two dehydration and two decomposition processes, and the final product is Er_2O_3 at 650°C with 37.18% weight residual (calcd 37.47%). For **II**, there were three stages: two dehydration processes and one decomposition, and at 550°C appeared the final product Er_2O_3. The results

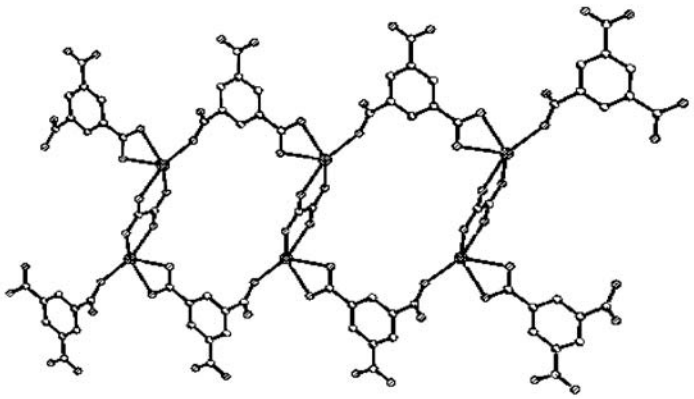

Fig. 2. Slightly slantwise 1D ladder in **I**.

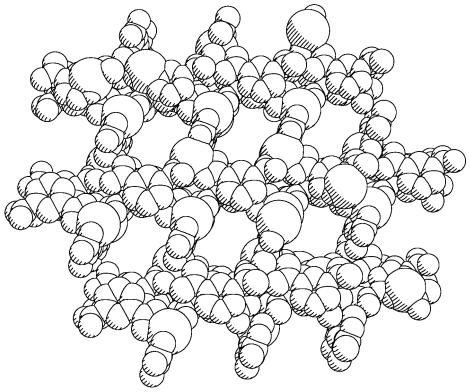

Fig. 3. Porous three-dimensional supermolecular framework in **I**.

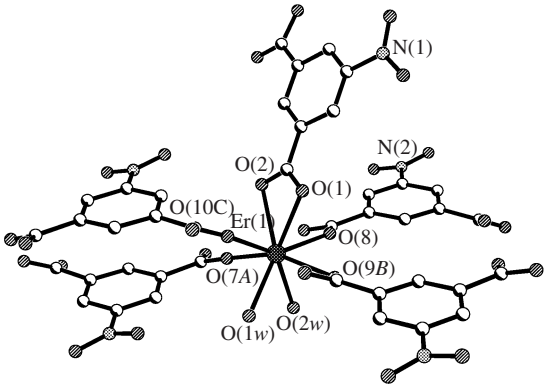

Fig. 4. Coordination environment of Er(III) in **II** (important bond lengths: Er(1)–O(7)^{i} 2.238(2); Er(1)–O(10)^{ii} 2.284(2); Er(1)–O(8) 2.315(2); Er(1)–O(9)^{iii} 2.343(2); Er(1)–O(2*w*) 2.372(3); Er(1)–O(1*w*) 2.386(2); Er(1)–O(1) 2.439(2); Er(1)–O(2) 2.459(2) Å and angle O(1)Er(1)O(2) 53.35(8)°; O(2*w*)Er(1)O(1*w*) 71.20(9)° (symmetry code: ^{i} $-x+1, -y+1, -z+1$; ^{ii} $x, y+1, z$; ^{iii} $-x, -y, -z+1$).

witnessed that the framework of **I** was more stable than that of **II**.

ACKNOWLEDGMENTS

This work was supported by the NNSF of China (grant no. 20771089), NNSF of Shaanxi Province (grant no. 2007B02), Shaanxi Physicochemical Key Laboratory, and Shaanxi Key Laboratory of Chemical Reaction Engineering.

REFERENCES

1. Braunstein, P., Matt, D., Nobel, D., *Chem. Rev.*, 1988, vol. 88, p. 747.
2. Beley, M., Collin, J.P., Ruppert, R., and Sauvage, J.P., *J. Am. Chem. Soc*., 1986, vol. 108, p. 7461.
3. Frölich, H.O., Schreer, H., *Z. Chem.* 1983, vol. 23, p. 348.
4. Evans, W.J., Seibel, C.A., and Ziller, J.W. *Inorg. Chem.* 1998, vol. 37, no. 4, p. 770.
5. Farrugia, L.J., Lopinski, S., Lovatt, P.A., and Peacock, R.D., *Inorg. Chem.* 2001, vol. 40, no. 3, p. 558.
6. Barret Adams, D.M.Y., Kahwa, I.A., Mague, J.T., *New J. Chem.*, 1998, vol. 22, p. 919.
7. Sheldrick, G.M., SHELXS-97, Program for X-ray Crystal Structure Determination, Göttingen (Germany): Univ. of Gottingen, 1997.
8. Sheldrick, G.M. SHELXL-97, Program for X-ray Crystal Structure Refinement, Göttingen (Germany): Univ. of Göttingen, 1997.
9. Sheldrick, G.M., SHELXTL, Version V., Madison (WI, USA): Siemens Industrial Automation Inc., 1997.
10. Shufeng Si., Chunhui Li., Ruji Wang, Yadong Li., *J. Mol. Struct*. 2004, vol. 703, no. 1–3, p.11.
11. Price, C.C. and Roberts, R.M., *J. Am. Chem. Soc*. 1946, vol. 68, no. 7, p. 1204.
12. Dongwon Min and Soon W. Lee, *Inorg. Chem. Commun.* 2002, vol. 5, no. 11, p. 978.
13. Yixia Ren, Sanping Chen, Gang Xie, et al., *Inorg. Chim. Acta*, 2006, vol. 359, p. 2047.