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Synthesis and crystal structures of cerium(IV) complexes with 8-quinolinolate and amine bis(phenolate) ligands

Li Li, Fugen Yuan*, Tingting Li, Yuan Zhou, Manman Zhang

School of Chemistry and Biochemistry, University of Science and Technology of Suzhou, Suzhou 215009, China

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1. Introduction

Cerium ion is special for its readily accessible tetravalent oxidation state as well as facile +4/+3 redox couple. Due to its unique redox chemistry, cerium(IV) complexes have been applied as versatile oxidative reagents in organic synthesis [1], photocatalytic oxidation [2], electrochemistry [3] and biochemistry [4]. There is an increasing demand for new and well-defined cerium(IV) species. Many types of Ce(IV) complexes have been reported such as $[{(Ph_2SiO)_2O}{K(THF)_2}]_2Ce(O^tBu)_2$ [5], $[{(Ph_2SiO)_2O}_2{(DME)KO^t}]_2Ce(O^tBu)_2$ Bu}{(Ph₂SiO₂)K}Ce]₂ [5], $p^{-t}Bu^{-calix}[4](OMe)_2(O)_2Ce(acac)_2$ [6], $Ce_3(\mu^3-O^tBu)_2(\mu-O^tBu)_3(O^tBu)_6$ [7], $Ce(L^1)_4$ (L¹ = 2,2,7-trimethyl-3,5-octanedione) [8], Ce(NN'₃)I [NN'₃³⁻ = N(CH₂CH₂NSiMe₂^tBu)₃³⁻] [9], CeCl[N(SiMe₃)₂]₃ [10], Ce(salfen)(O^tBu)₂ (Salfen = ferrocene Schiff base) [11], Ce(L²)X (X = Cl [12], NO₃ [12], BPh₄ [13], N₃ [13]; $L^2H_3 = N\{CH_2CH_2N = CH(C_6H_2-{}^tBu_2-3,5-OH-2)\}_3\}$, $Ce(L^3)_2$ (L^3) $H_2 = N_N - bis(3.5 - di - tert - butyl salicylidene) ethylenediamine) [14],$ $(L^{4}H_{2} = N, N'-bis(2-hydroxybenzyl)ethane-1,2 Ce(L^4)_2 \cdot CHCl_3$ diamine) [15], $Ce(L^5)_4$ ($L^5H = C\{(N^iPr)CHCHN\}CH_2CMe_2OH\}$ [16], Ce{C₈H₄(SiⁱPr₃-1,4)₂}₂ [17], (C₅H₅)₃CeCl [18], [p-MeOC₆H₄C(NSiMe₃)₂]₃CeCl [18], etc. It is noteworthy that the ligands are mainly O/N species, and Schiff bases are usually used during the synthesis of Ce(IV) aryloxide complexes.

Actually, 8-hydroxyquinoline and amine bis(phenol) are chemically more stable than Schiff bases. They have been widely used in coordination with lanthanide metals [19,20]. The formation of Ce(IV) 8-quinolinolate complex has been known to analytical chemists for a long time [21]. However, only the composition

ABSTRACT

Two cerium(IV) complexes of Ce(OQ)₄ (1) (HOQ = 8-hydroxyquinoline) and Ce(L)₂·DME (2·DME) (LH₂ = $Me_2NCH_2CH_2CH_2CH_2CH_2C_15$ - $^{t}Bu_2$ -C₆H₂-2-OH)₂) have been synthesized and characterized by elemental analysis, infrared spectra and X-ray crystallography. Complex 1 is a new type of homoleptic 8-quinolinolate lanthanide complex and its overall geometry is like a four-wing-waterwheel. Complex 2 has two tridentate (ONO) amine bis(phenolate) ligands with their terminal N atoms in side-arms without participating in coordination. Both of 1 and 2 can catalyze the oxidation of benzyl alcohol. The conversion of benzyl alcohol by 2 is higher than that by 1 under comparable conditions.

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and solubility of this complex were determined. Its structure has not been established up to date. Herein we report the synthesis and crystal structures of $Ce(OQ)_4$ (1) (HOQ = 8-hydroxyquinoline) and $Ce(L)_2$ ·DME (2·DME) (LH₂ = Me₂NCH₂CH₂CH₂N{CH₂-(3,5-^tBu₂-C₆H₂-2-OH)}₂). Complex 1 is a new type of homoleptic 8quinolinolate lanthanide complex, and the cerium(IV) ion in complex 2 has low coordination number, because the terminal N atoms in side-arms do not participate in coordination. Finally, the catalytic activity of 1 and 2 for oxidation of benzyl alcohol was tested.

2. Experimental

2.1. General

Tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) were distilled from sodium/benzophenone. Ceric ammonium nitrate (CAN) was dried at 110 °C. Sodium *tert*-butoxide (^tBuONa) was prepared by reaction of *tert*-butanol with sodium hydride (NaH) in THF. Ce(SO₄)₂·4H₂O and 8-hydroxyquinoline were purchased from commercial sources and used as received without further purification. Amine bis(phenol) LH₂ was synthesized according to the literature procedure [22]. Carbon, hydrogen and nitrogen analyses were carried out by direct combustion on an EA1110-CHNSO elemental analyzer. Cerium(IV) elemental analysis was carried out by complexometric titration as normal except that an excess of ascorbic acid was added to the solution before the titration to reduce all Ce⁴⁺ to Ce³⁺ [23]. The IR spectra were recorded on a Perkin Elmer Spectrum BXII spectrometer. Melting point was taken in a sealed argon-filled capillary and uncorrected.





^{*} Corresponding author. Tel.: +86 512 68418483; fax: +86 512 68418935. *E-mail address:* yuanfugensuzhou@163.com (F. Yuan).

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2.2. Synthesis and characterization of 1

To an aqueous solution (20 mL) of Ce(SO₄)₂·4H₂O (0.392 g, 0.970 mmol) was added an alcohol solution (20 mL) of 8-hydroxyquinoline (0.564 g, 3.884 mmol). Brown precipitate produced immediately. The mixture was stirred, and a NaOH solution (1.0 mol/L) was slowly dropped into it until pH value was about 7. During the process, more precipitate was produced. Black brown powders of **1** (0.516 g, 74.2%) could be obtained by filtration. Crystals suitable for X-ray diffraction analysis were obtained by recrystallization of the powder in a 2-methoxyethanol solution at 25 °C. *Anal.* Calc. for C₃₆H₂₄CeN₄O₄: C, 60.32; H, 3.35; N, 7.82; Ce, 19.56. Found: C, 59.60; H, 3.31; N, 7.78; Ce, 19.41%. M.p. >250 °C. IR (KBr, cm⁻¹) 3434(s), 2364(m), 2346(m), 1599(m), 1493(m), 1461(m), 1377(m), 1315(s), 1270(m), 1234(s), 1105(s), 823(w), 786(w), 733(m), 608(w), 508(w), 484(w).

2.3. Synthesis and characterization of 2

The synthesis was carried out under an atmosphere of argon using Schlenk techniques because the precursor Ce(O^tBu)₄ is very sensitive toward moisture and air. A THF solution of Ce(O^tBu)₄ (2.16 mmol) was prepared in situ from ceric ammonium nitrate (CAN) (1.184 g, 2.16 mmol) and ^tBuONa (12.96 mmol) in THF according to the literature method [23]. It was added into a THF solution of LH₂ (2.328 g, 4.32 mmol), the mixture immediately turned from orange to brown black. It was stirred for a day, and then evaporated to dryness. DME solvent was condensed in to dissolve the residue. After centrifugation, a clear black solution was got. It was frozen in the refrigerator for 3 d. Black crystals of 2.DME (1.168 g, 41.7%) were produced. M.p. 226.8 °C. Anal. Calc. for C₇₄ H₁₂₂CeN₄O₆: C, 68.20; H, 9.37; N, 4.30; Ce, 10.76. Found: C, 68.00; H, 9.32; N, 4.22; Ce, 10.80%. IR (KBr, cm⁻¹) 3435(m), 2915(s), 2865(m), 2813(w), 2777(w), 1624(w), 1466(s), 1439(m), 1413(m), 1390(w), 1360(w), 1307(w), 1258(s), 1239(s), 1204(w), 1168(w), 1129(w), 876(w), 834(m), 807(w), 745(m), 535(m), 455(w).

2.4. Determination of crystal structures

Data collection for complexes **1** and **2** were performed on a APEX II 4 K CCD area detector equipped with a graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) by using the ω -scan mode at room temperature. All absorption corrections were applied using the CRYSTALCLEAR program [24]. The structures were solved by direct methods for **1** and patterson methods for **2**, respectively. The cerium metal atoms were located from the e-maps, and other non-hydrogen atoms were derived from the successive difference Fourier peaks. The hydrogen atoms of the ligands were positioned geometrically, and allowed to ride on their parent C atoms. The hydrogen atoms of complex **1** were not located due to the orientational disorder of 8-quinolinolates [25]. Two structures were refined on F^2 by full-matrix least-squares using the SHELXTL-97 program package [26]. Summary of the crystallographic data for **1** and **2** are given in Table 1.

2.5. Catalytic oxidation of benzyl alcohol

Complex, PhCH₂OH and NaBrO₃ were charged to a round bottomed flask. The mixture was stirred in a thermostat bath for a certain time. It was cooled down and extracted for three times with ethylacetate. The extracted sample was analyzed by a gas chromatograph (GC) to determine the contents of benzaldehyde (with nitrobenzene as internal standard) and benzoic acid (with dimethyl phthalate as internal standard).

Table 1

Summary of the crystallographic data for **1** and **2**.

Complex	1	2.DME
Empirical formula	CaeHa4CeN4O4	C74H122CeN4O6
Formula weight	716.71	1303.88
Temperature (K)	296	296
Crystal system	monoclinic	triclinic
Space group	P2(1)/n	ΡĪ
Crystal size (mm)	$0.18 \times 0.14 \times 0.12$	$0.35 \times 0.23 \times 0.18$
a (Å)	9.986(4)	18.4201(14)
b (Å)	9.778(4)	21.3300(16)
c (Å)	16.200(6)	21.4870(17)
α (°)	90	100.4890(10)
β (°)	106.783(4)	96.2760(10)
γ (°)	90	113.2860(10)
V (Å ³)	1514.4(10)	7469.8(10)
Ζ	2	4
$D_{\text{calc}} (\text{g cm}^{-3})$	1.572	1.159
F(000)	716	2800
μ (mm $^{-1}$)	1.550	0.659
 θ range for data collection (°) 	2.13-27.55	1.23-27.45
Total No. of reflections	12761	65702
No. of unique reflections	3468	33 385
Data/restraints/ parameters	3468/290/204	33385/4060/1516
Index range	$-12 \leqslant h \leqslant 12$	$-23 \leqslant h \leqslant 23$
	$-11 \leq k \leq 12$	$-27 \leqslant k \leqslant 27$
	$-20 \leqslant l \leqslant 20$	$-27 \leqslant l \leqslant 27$
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0564$,	$R_1 = 0.0537$,
	$wR_2 = 0.1344$	$wR_2 = 0.1230$
R indices (all data)	$R_1 = 0.0811$,	$R_1 = 0.1008,$
	$wR_2 = 0.1470$	$wR_2 = 0.1494$
Goodness-of-fit (GOF)	1.126	1.053
Residual peaks (e/ų)	0.816, -0.881	1.320, -0.863



Fig. 1. Molecular structure of complex **1** showing 30% probability ellipsoids with H atoms omitted for clarity.

3. Results and discussion

3.1. Synthesis and crystal structure of 1

8-Hydroxyquinoline is a classical chelating reagent for lanthanides. Although complexes of $Ln(OQ)_3$ (Ln = Sc, La, Pr, Eu, Yb) were synthesized early [27], they are unfortunately insoluble in any

Table 2 Selected bond lengths (Å) and angles (°) for complex 1.

Ce(1)-O(1)	2.263(10)	Ce(1)-O(1')	2.193(9)
Ce(1)-O(2)	2.263(10)	Ce(1)-O(2')	2.222(9)
Ce(1)-N(1)	2.612(12)	Ce(1)-N(1')	2.612(12)
Ce(1)-N(2)	2.644(10)	Ce(1)-N(2')	2.644(10)
O(1')-Ce(1)-O(2')	57.1(4)	O(1') -Ce(1)-O(2')	122.9(4)
O(1')-Ce(1)-O(2)	55.0(4)	O(1')-Ce(1)-O(2)	125.0(4)
O(2')-Ce(1)-O(2)	84.6(4)	O(2')-Ce(1)-O(2)	95.4(4)
O(1')-Ce(1)-C(1')	154.3(4)	O(2)-Ce(1)-C(1')	106.4(4)

Symmetry code: 2 - x, 2 - y, -z.



solvents. In 2005, Deacon's group obtained accidentally the first homoleptic $Ho_3(OQ)_9$ ·HOQ [25], which is the only structure of homoleptic 8-quinolinolate lanthanide complex to the best of our knowledge. The coordination of 8-quinolinolate with Ce(IV) has not been reported yet.

When $Ce(SO_4)_2$ aqueous solution was mixed with 8-hydroxyquinoline, the color of the mixture changed from yellow to black immediately, and black powders precipitated at the same time, which indicated that the reaction occurred. When the pH value of the mixture was adjusted with a NaOH solution from acidity to neuter, more black precipitates could be obtained. When pH arrived 7, the yield reached maximum of 74.2%. The elemental analyses and the IR spectra were in agreement with the formation of complex **1**. The IR absorption bands at 1376, 1460, 1493, and 1599 cm⁻¹ are assigned to C=N and C=C stretching vibration frequencies in 8-quinolinolate ligand [28,19c], and the absorptions at 484 and 733 cm⁻¹ are attributed to the Ce–O vibration [29]. Fortunately, complex **1** is soluble in 2-methoxyethanol and can be crystallized in the solvent. The molecular structure of **1**, determined by X-ray crystallography, is shown in Fig. 1. The selected bond lengths and angles are listed in Table 2. The reaction process is expressed in Scheme 1.

As shown in Fig. 1, a cerium ion is surrounded by four 8quinolinolate ligands. Four central axes of quinolinolate ligands are located in a plane with the cerium ion. The four ligands approximately divide a circle into four equipartitions, as the dihedral angles between the neighbor 8-quinolinolate planes are 89.5°. The overall geometry is like a four-wing-waterwheel. Each 8quinolinolate group is coordinated bisdentately to the cerium ion *via* nitrogen and oxygen atoms. The coordination number of cerium is eight. The 8-quinolinolate ligands in complex **1** display orientational disorder with 50% occupancy of both disordered forms (Fig. 2). This phenomenon is also observed in other 8quinolinolate metal complexes of Ho₃(OQ)₉·HOQ [25], Hf(OQ)₄· C₃H₇NO·H₂O [30] and LaNi₂(OQ)₇ [19f].

The selected bond lengths and angles for complex **1** are presented in Table 2. The oxidation state of cerium was calculated to be 4.1 according to the bond valence sum [31]. The Ce–O bond lengths (2.193(9)–2.263(10) Å) are consistent with those in Ce(L³)₂ (2.237(3)–2.258(4) Å) [14] and Ce(L⁴)₂·CHCl₃ (2.188(4)–2.239(4) Å) [15]. The Ce–N bond lengths (2.612(12)–2.644(10) Å) are comparable with those in Ce(L²)NO₃ (2.569(2)–2.808(2) Å) [12] and Ce(L⁴)₂·CHCl₃ (2.603(4)–2.628(4) Å) [15].

3.2. Synthesis and crystal structure of 2

Complex **2** was synthesized by protolysis of $Ce(O^tBu)_4$ with amine bis(phenol) (LH₂). Crystals suitable for X-ray diffraction analysis were obtained from the DME solution. The molecular structure of **2** is shown in Fig. 3, and the selected bond lengths and angles are listed in Table 3. The reaction process is expressed in Scheme 2.

According to X-ray results (Fig. 3), a cerium ion is coordinated by two tridentate (ONO) amine bis(phenolate) ligands. Two terminal tertiary N atoms in the side arms do not participate in coordination with the cerium. This may account for the steric hindrance of bulky *tert*-butyl substituents. The coordination number of cerium ion is six: four oxygen atoms and two nitrogen atoms. The



Fig. 2. The two disordered forms (equal occupancy) of ligand in complex 1.



Fig. 3. Molecular structure of complex 2 showing 30% probability ellipsoids with H atoms omitted for clarity.

 Table 3

 Selected bond lengths (Å) and angles (°) for complex 2.

_				
	Ce(1)-O(1)	2.140(3)	Ce(1)-O(2)	2.160(3)
	Ce(1)-O(3)	2.139(3)	Ce(1)-O(4)	2.142(3)
	Ce(1)-N(1)	2.598(3)	Ce(1)-N(2)	2.596(3)
	O(1)-Ce(1)-O(2)	148.6(10)	O(1)-Ce(1)-O(4)	92.1(11)
	O(1)-Ce(1)-N(1)	73.8(10)	O(1)-Ce(1)-N(2)	106.3(11)
	O(2)-Ce(1)-N(1)	75.1(11)	O(2)-Ce(1)-N(2)	104.9(11)
	O(3)-Ce(1)-O(1)	95.0(11)	O(3)-Ce(1)-O(2)	90.1(11)
	O(3)-Ce(1)-O(4)	149.7(11)	O(3)-Ce(1)-N(1)	106.7(10)
	O(3)-Ce(1)-N(2)	75.0(10)	O(4)-Ce(1)-O(2)	99.0(11)
	O(4)-Ce(1)-N(1)	103.6(10)	O(4)-Ce(1)-N(2)	74.7(10)
	N(1)-Ce(1)-N(2)	178.3(10)		

coordination polyhedron around cerium atom can be described as a distorted octahedron (Fig. 4).

The oxidation state of cerium in complex **2** was calculated to be 4.4 according to the bond valence sum [31]. The Ce–O bond lengths (2.139(3)-2.160(3) Å) are consistent with those in Ce(L⁵)₄ (2.130(4)-2.140(4) Å) [16]. They are also comparable with those in eight-coordinate Ce(L³)₂ (2.237(3)-2.258(4) Å) [14] when the

ionic radius difference between six-coordinate Ce⁴⁺ (0.87 Å) and eight-coordinate Ce⁴⁺ (0.97 Å) was taken into account [32]. The Ce–N bond lengths (average 2.597 Å) are a little shorter than that in eight-coordinate Ce(L²)Cl (2.774(2) Å) [12] when the ionic radius difference was taken into account, but comparable with that in seven-coordinate Ce(L²)BPh₄ (2.6548(19) Å) [13]. Three atoms of N(1), Ce(1) and N(2) are nearly in a line (178.29(10)°). The bite angles of O(1)–Ce(1)–O(2) and O(3)–Ce(1)–O(4) are typical for Ce(IV) complexes [12–14].

3.3. Catalytic activity of 1 and 2

The catalytic oxidation of benzyl alcohol in the presence of **1** and **2** was tested. In the reaction complexes of **1** and **2** acted as the catalyst, and sodium bromate (NaBrO₃) did as the oxidant. Although complexes of **1** and **2** are reactive toward benzyl alcohol, the reactions are stoichiometric. The combination of Ce(IV) complex with sodium bromate leads to the recycle of Ce(IV) species from the Ce(III) compound (Eq. (1)) [1a]. It is noteworthy that sodium bromate itself, without Ce(IV) catalyst, is unable to oxidize benzyl alcohol. Both of **1** and **2** in the presence of 1 equivalent of



Scheme 2.



Fig. 4. The octahedron geometry around a cerium ion for complex 2.

Table 4

Oxidation of benzyl alcohol catalyzed by 1 and 2.

	≻−сн	$\begin{array}{c} \text{cat. (4-10 mol\%)} \\ \text{NaBrO}_3 (1 \text{ eqiv}) \\ \hline \\ \text{no solvent} \end{array}$		-CHO + ⟨	Соон
Entry	Cat.	n(cat./PhCH ₂ OH)	Temp.	Yield of	Yield of
		(molar ratio)	(°C)	PhCOOH (%)	PhCHO (%)
1	1	0.04	80	0.0	0.0
2	1	0.10	80	0.6	4.3
3	1	0.10	100	4.4	6.4
4	1	0.15	100	10.5	7.6
5	2	0.10	60	27.6	5.2
6	2	0.10	80	61.5	7.3

Conditions: oxidation time 2.0 h, in bulk, $n(NaBrO_3)/n(PhCH_2OH) = 1/1$ (molar ratio).

sodium bromate (referred to benzyl alcohol) can catalyze the oxidation reaction. Results are summarized in Table 4. The conversion of benzyl alcohol by complex **2** is higher than that by complex **1** under comparable conditions, which implies that the oxidation property of a cerium complex is affected by its coordinating ligand. Hence it is possible obtain proper catalyst by apt selection of the ligand. The research is currently in progress.

$$4Ce(III) + BrO_{3}^{-} + 5H^{+} = 4Ce(IV) + HOBr + 2H_{2}O$$
(1)

4. Conclusions

In summary, two Ce(IV) complexes with 8-quinolinolate and amine bis(phenolate) ligands were synthesized and characterized by elemental analysis, infrared spectra and X-ray crystallography. Homoleptic Ce(OQ)₄ is a monomer, whose structure is quite different from that of Ho₃(OQ)₉·HOQ [25]. The Ce(IV) ion in Ce(L)₂ has coordination number of six, because the terminal N atoms in side-arms do not participate in coordination. Complexes **1** and **2** can catalyze the oxidation of benzyl alcohol. The coordinating ligand has a great influence upon the catalytic property.

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Appendix A. Supplementary material

CCDC 872689 and CCDC 873855 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2012.11.020.

References

- [1] (a) V. Sridharan, J.C. Menéndez, Chem. Rev. 110 (2010) 3805;
 - (b) A.K. Das, Coord. Chem. Rev. 213 (2001) 307; (c) V. Nair, L. Balagopal, R. Raian, I. Mathew, Acc. Chem. Res. 37 (2004) 21:
 - (d) J. Dziegiec, S. Domagala, Trends Inorg. Chem. 8 (2005) 43;
 - (e) S.D. Burke, R.L. Danheiser, Handbook of Reagents for Organic Synthesis:
 - Oxidizing and Reducing Agents, vol. 3, John Wiley & Sons Ltd., West Sussex, UK, 1999.
- [2] (a) J.D. Blakemore, N.D. Schley, D. Balcells, J.F. Hull, G.W. Olack, C.D. Incarvito, O. Eisenstein, G.W. Brudvig, R.H. Crabtree, J. Am. Chem. Soc. 132 (2010) 16017;

(b) D.J. Wasylenko, C. Ganesamoorthy, M.A. Henderson, C.P. Berlinguette, Inorg. Chem. 50 (2011) 3662;

- (c) Y.M. Lee, S.N. Dhuri, S.C. Sawant, J. Cho, M. Kubo, T. Ogura, S. Fukuzumi, W. Narn, Angew. Chem., Int. Ed. 48 (2009) 1803.
- [3] (a) A.L. Gal, S. Abanades, J. Phys. Chem. C 116 (2012) 13516;
- (b) T. Masuda, H. Fukumitsu, K. Fugane, H. Togasaki, D. Matsumura, K. Tamura, Y. Nishihata, H. Yoshikawa, K. Kobayashi, T. Mori, K. Uosaki, J. Phys. Chem. C 116 (2012) 10098;
- (c) D. Joung, V. Singh, S. Park, A. Schulte, S. Seal, S.I. Khondaker, J. Phys. Chem. C 115 (2011) 24494.
- [4] (a) Y. Miyajima, T. Ishizuka, Y. Yamamoto, J. Sumaoka, M. Komiyama, J. Am. Chem. Soc. 131 (2009) 2657;
 - (b) R.T. Kovacic, J.T. Welch, S.J. Franklin, J. Am. Chem. Soc. 125 (2003) 6656;
- (c) Y. Aiba, T. Lönnberg, M. Komiyama, Chem. -Asian J. 6 (2011) 2407.
 [5] S. Giessmann, S. Blaurock, V. Lorenz, F.T. Edelmann, Inorg. Chem. 46 (2007) 8100
- [6] J. Gottfriedsen, D. Dorokhin, Z. Anorg. Allg. Chem. 631 (2005) 2928.
- [7] P.L. Arnold, I.J. Caselya, S. Zlatogorsky, C. Wilson, Helv. Chim. Acta 92 (2009) 2291.
- [8] W.C. Andersen, B.C. Noll, S.P. Sellers, L.L. Whildin, R.E. Sievers, Inorg. Chim. Acta 336 (2002) 105.
- [9] C. Morton, N.W. Alcock, M.R. Lees, I.J. Munslow, C.J. Sanders, P.J. Scott, J. Am. Chem. Soc. 121 (1999) 11255.
- [10] O. Eisenstein, P.B. Hitchcock, A.G. Hulkes, M.F. Lappert, L. Maron, Chem. Commun. 17 (2001) 1560.
- [11] E.M. Broderick, P.L. Diaconescu, Inorg. Chem. 48 (2009) 4701.
- [12] P. Dröse, J. Gottfriedsen, Z. Anorg. Allg. Chem. 634 (2008) 87.
- [13] P. Dröse, J. Gottfriedsen, C.G. Hrib, P.G. Jones, L. Hilfert, F.T. Edelmann, Z. Anorg. Allg. Chem. 637 (2011) 369.
- [14] J. Gottfriedsen, M. Spoida, S. Blaurock, Z. Anorg. Allg. Chem. 634 (2008) 514.
- [15] S.P. Yang, L.J. Han, D.Q. Wang, B. Wang, Acta Crystallogr. E63 (2007) m2777.
- [16] I.J. Casely, S.T. Liddle, A.J. Blake, C. Wilsonc, P.L. Arnold, Chem. Commun. (2007) 5037.
- [17] G. Balazs, F.G.N. Cloke, J.C. Green, R.M. Harker, A. Harrison, P.B. Hitchcock, C.N. Jardine, R. Walton, Organometallics 26 (2007) 3111.
- [18] P. Dröse, A.R. Crozier, S. Lashkari, J. Gottfriedsen, S. Blaurock, C.G. Hrib, C. Maichle-Mössmer, C. Schädle, R. Anwander, F.T. Edelmann, J. Am. Chem. Soc. 132 (2010) 14046.
- [19] (a) G.B. Deacon, C.M. Forsyth, P.C. Junk, A. Urbatsch, Eur. J. Inorg. Chem. (2010) 2787;
 (b) L.N. Sun, H.J. Zhang, J.B. Yu, S.Y. Yu, C.Y. Peng, S. Dang, X.M. Guo, J. Feng, Langmuir 24 (2008) 5500;
 (c) F. Artizzu, P. Deplano, L. Marchiò, M.L. Mercuri, L. Pilia, A. Serpe, F. Quochi,

 R. Orrù, F. Cordella, F. Meinardi, R. Tubino, A. Mura, G. Bongiovanni, Inorg. Chem. 44 (2005) 840;
 (d) A. O'Riordan, R.V. Deun, E. Mairiaux, S. Moynihan, P. Fias, P. Nockemann, K.

(e) R.V. Deun, P. Fias, P. Nockemann, A. Schepers, T.N. Parac-Vogt, K.V. Hecke,
 (e) R.V. Deun, P. Fias, P. Nockemann, A. Schepers, T.N. Parac-Vogt, K.V. Hecke,

L.V. Meervelt, K. Binnemans, Inorg. Chem. 43 (2004) 8461; (f) G.B. Deacon, C.M. Forsyth, P.C. Junk, S.G. Leary, New J. Chem. 30 (2006) 592.

[20] (a) O. Wichmann, R. Sillanpää, A. Lehtonen, Coord. Chem. Rev. 256 (2012) 371;
 (b) Y. Yao, M. Ma, X. Xu, Y. Zhang, Q. Shen, W.-T. Wong, Organometallics 24 (2005) 4014;

(c) K. Nie, X. Gu, Y. Yao, Y. Zhang, Q. Shen, Dalton Trans. 39 (2010) 6832;

(d) C.E. Willans, M.A. Sinenkov, G.K. Fukin, K. Sheridan, J.M. Lynam, A.A. Trifonov, F.M. Kerton, Dalton Trans. (2008) 3592;

(e) E.E. Delbridge, D.T. Dugah, C.R. Nelson, B.W. Skelton, A.H. White, Dalton Trans. (2007) 143;

(f) H.E. Dyer, S. Huijser, A.D. Schwarz, C. Wang, R. Duchateau, P. Mountford, Dalton Trans. (2008) 32;

(g) M. Ma, X. Xu, Y. Yao, Y. Zhang, Q. Shen, J. Mol. Struct. 740 (2005) 69. [21] (a) K.B. Yatsimirskii, N.A. Kostromina, Z.A. Sheka, N.K. Davidenko, E.E. Kriss, V.I. Ermolenko, Chemistry of Rare-Earth Element Complex Compounds (Khimiya

Kompleksnych Soedinenii Redkozemel'nikh Elementov) Naukova Dumka, Kiev, 1966, p. 493 (in Russian).; (b) J.E. Roberts, M.J. Ryterband, Anal. Chem. 37 (1965) 1585;

(c) Z. Marczenko, M. Balcerzak, Separation, Preconcentration, and Spectrophotometry in Inorganic Analysis, Elsevier BV, New York, 2000. 521;
(d) I.M. Korenman, A.A. Tumanov, V.M. Sorokina, Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol. 3 (1960) 580 (in Russian).

- [22] E. Tshuva, I. Goldberg, M. Kol, Z. Goldschmidt, Inorg. Chem. 40 (2001) 4263.
- [23] W.J. Evans, T.J. Deming, J.M. Olofson, J.W. Ziller, Inorg. Chem. 28 (1989) 4027.
- [24] (a) G.M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structure, University of Göttingen, Germany, 1997.;

(b) G.M. Sheldrick, SHELXS-97, Program for the Refinement of Crystal Structure, University of Göttingen, Germany, 1997.

- [25] S.G. Leary, G.B. Deacon, P.C. Junk, Z. Anorg. Allg. Chem. 631 (2005) 2647.
- [26] G.M. Sheldrick, Acta Crystallogr. A64 (2008) 112.
- [27] W.W. Wendlandt, Anal. Chim. Acta 15 (1956) 109.
- [28] (a) H.F. Aly, F.M. Kerim-Abdel, A.T.J. Kandil, J. Inorg. Nucl. Chem. 33 (1971) 4340;
- (b) M. Cölle, S. Forero-Lenger, J. Gmeiner, W. Brütting, Phys. Chem. Chem. Phys. 5 (2003) 2958.
- [29] (a) P. Fias, Lanthanide(III) quinolinates and phenalenonates: a structural and spectroscopic investigation, Degree Thesis, Faculteit Wetenschappen, Departement Chemie, 2005.;
- (b) R.G. Charles, H. Freiser, R. Friedel, L.E. Hilliard, W.D. Johnston, Spectrochim. Acta 8 (1956) 1.
- [30] J.A. Viljoen, H.G. Visser, A. Roodt, Acta Crystallogr. E66 (2010) m603.
- [31] G.J. Palenik, S.Z. Hu, Inorg. Chim. Acta 362 (2009) 4740.
- [32] R.D. Shannon, Acta Crystallogr. A32 (1976) 751.