ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2019, Vol. 45, No. 3, pp. 238–243. © Pleiades Publishing, Ltd., 2019.

Two Rare-Earth Complexes (Sm, La) Based on a Carbon-Bridged Bis(phenolate): Synthesis and Crystal Structures[1]

K. Wang[a], X. M. Luo[a], P. Chen[b], Y. Q. Liu[a], B. Liu[c], H. J. Jiang[b], and Y. C. Ju[b, *]

[a] *School of Basic Medical Sciences, Nanjing Medical University, Nanjing, Jiangsu Province, 211166 P.R. China*

[b] *School of Pharmacy, Nanjing Medical University, Nanjing, Jiangsu Province, 211166 P.R. China*

[c] *Key Laboratory of Organic Synthesis of Jiangsu Province and Suzhou Key Laboratory of Macromolecular Design and Precision Synthesis, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Dushu Lake Campus, Suzhou, Jiangsu Province, 215123 P.R. China*

**e-mail: jyc2003@njmu.edu.cn*

Received March 16, 2018; revised October 17, 2018; accepted October 30, 2018

Abstract—Two rare earth metal complexes based on the carbon-bridged bis(phenolate) ligand, 2,2'-methylene-bis(6-*tert*-butyl-4-methyl-phenoxo) (LH_2), have been synthesized. Reaction of LH_2 with $(C_5H_5)_3Sm(THF)$ in a 1.5 : 1 molar ratio in THF at 50°C produced rare earth metal bis(phenolate) complex $(C_5H_5)Sm(L)(THF)_2$ (**I**) in almost quantitative yields. Complex **I** reacted with 0.5 molar ratio of LH_2 in toluene at 80°C afforded $(L)Sm(LH)(THF)_2$ (**II**) as the final product in good yield. Reaction of LNa_2 with $LaCl_3$ in a 2 : 1 molar ratio in THF at room temperature produced hetero-nuclear rare earth metal bis(phenolate) complex $(L)La(LH)(THF)_2Na(THF)_2$ (**III**). In addition, **II** and **III** were characterized by X-ray single-crystal diffraction analysis (CIF file CCDC nos. 1500917 (**II**) and 1826699 (**III**)) as well as characterizations including elemental analyses and IR spectra of both complexes. Furthermore, detail reasons of the difference of structures are presented. The ionic radii of the rare earth metal plays a significant role in the structure difference of two complexes.

Keywords: rare-earth, bis(phenolate), synthesis, structure

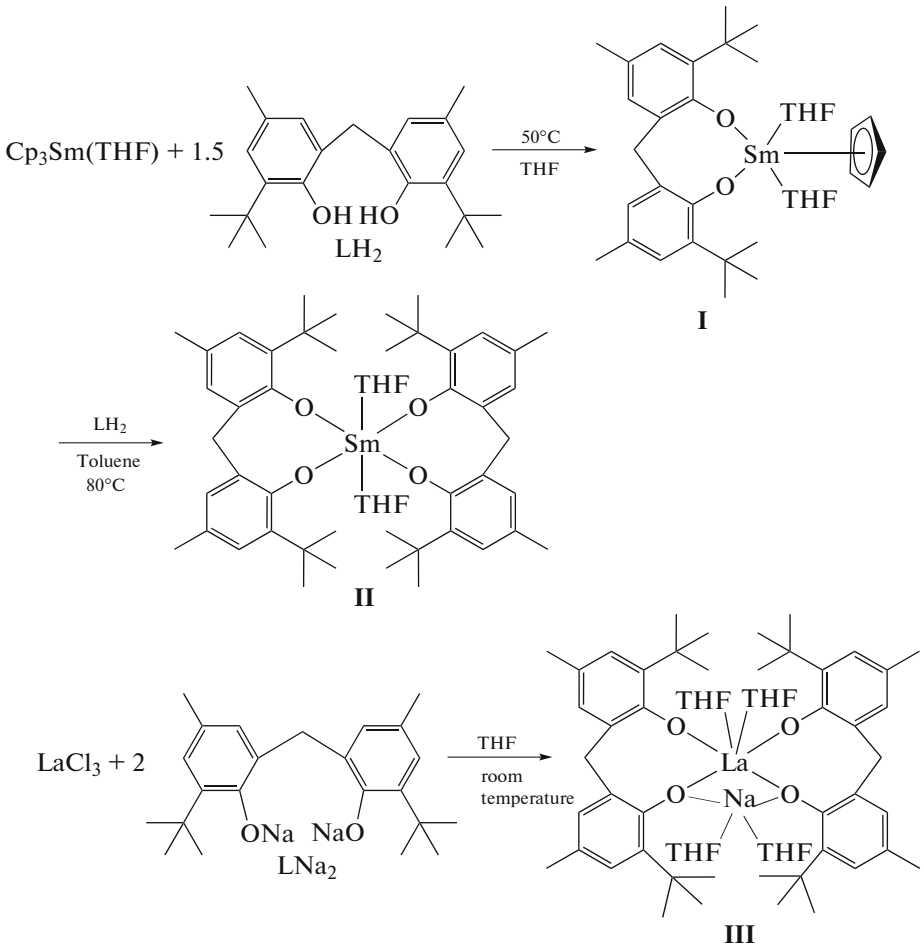
DOI: 10.1134/S1070328419030114

INTRODUCTION

Organometallic complexes remain a highly utilized and effective option in organic and polymer synthesis [1–3]. After those organometallic complexes bearing Cp-type ligands were widely used these years [4, 5], great efforts have been focused on unraveling the mode of action of different ligands [6, 7]. In this connection, ligands with oxygen donor atoms have received much attention. Among those, carbon-bridged bis(phenol)s, typically 2,2'-methylene-bis(6-*tert*-butyl-4-methyl-phenoxo) (LH_2), is designed to act as a dianionic ligand and bond with thehard Ln^{3+} ions [8]. Therefore, LH_2 are expected to stabilize rare-earth metal complexes. In fact, studies of organometallic complexes containing LH_2 have unveiled new catalytic activities for the polymerization of α-olefins in the presence of MAO [9], for the controllable polymerization of propylene oxide [10] and ε-caprolactone [11]. Moreover, as the ongoing interest in bis(phenolate) lanthanide chemistry [8, 12–15], the application of LH_2 as ancillary ligands in lanthanide chemistry impel us to find out the reactivity of LH_2 and reveal the relationship between structure and ionic radii.

We have synthesized and structurally characterized complexes $(L)Sm(LH)(THF)_2$ (**II**) and $(L)La(LH)(THF)_2Na(THF)_2$ (**III**) by X-ray single-crystal diffraction analysis. We explore the reactivity of LH_2 and LNa_2 to rich the contents of organo-lanthanide structural chemistry. Further, we clarify the reasons of ionic radii by comparison withthe structures of **II** and **III**. The syntheses of complexes **II** and **III** are given in Scheme 1:

[1] The article is published in the original.



Scheme 1.

EXPERIMENTAL

Materials and measurements. Standard Schlenk techniques were involved in all manipulations, using a purified argon atmosphere. Solvents were degassed and distilled from sodium benzophenone ketyl under argon before use. Lanthanide analyses were performed by EDTA titration with an xylenol orange indicator and hexamine buffer [16]. Carbon and hydrogen analyses were performed by direct combustion with a Carlo-Erba EA-1110 instrument. The IR spectra were recorded with a Nicolet-550 FT-IR spectrometer as KBr pellets. The ^{1}HNMR spectra were acquired on a Bruker DRX-400 spectrometer at 298 K. The uncorrected melting points of crystalline samples in sealed capillaries (under argon) are reported as ranges.

Synthesis of complex I, II. A THF solution (30 mL) containing LH_2 (1.12 g, 3.3 mmol) was slowly added to a THF (25 mL) solution of $(C_5H_5)_3Sm(THF)$ (0.814 g, 2.2 mmol). The reaction mixture was stirred for 6 h at 50°C, and then the solvent was removed under vacuum. Toluene (50 mL) was added to extract the product, and light yellow microcrystals were obtained (1.39 g, 91% based on lanthanum) from 14 mL toluene at −5°C, m.p. 189–192°C (decomp.).

For $C_{36}H_{51}O_4Sm$ (**I**, M = 698.16)

Anal. calcd., %	C, 61.93	H, 7.36	Sm, 21.54
Found, %	C, 61.38	H, 7.08	Sm, 21.13

IR (KBr; ν_{max}, cm^{-1}): 2965 s, 2917 s, 2870 s, 1615 m, 1458 vs, 1413 s, 1362 s, 1250 s, 1204 s, 1130 m, 1035 m, 913 w, 854 m, 729 m. ^{1}H NMR (400 MHz; C_6D_6; 25°C; δ, ppm): 1.47 (18H, $C(CH_3)_3$), 1.89 (24H, THF), 2.22 (6H, $ArCH_3$), 3.42 (2H, CH_2), 3.88 (4H, CH_2), 6.39 (2H, CH), 6.56 (2H, CH), 7.56 (2H, Ar), 7.76 (2H, Ar).

To a toluene solution 35 mL of **I** (1.39 g, 1.70 mmol) was added LH_2 (0.286 g, 0.85 mmol) in toluene. The reaction mixture was stirred 36 h at 80°C, and the solvent was removed under vacuum. *N*-Hexane (40 mL) was added to precipitate the product. The power obtained was dissolved in THF–toluene solution (1 : 1, 50 mL), and colorless microcrystals were

Table 1. Crystallographic data and structure refinements for **II** and **III**

Parameter	Value	
	II	**III**
T, K	193(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$C2/c$
a, Å	13.0584(11)	18.236(2)
b, Å	37.599(3)	17.972(2)
c, Å	15.0466(13)	18.597(2)
β, deg	106.483(2)	96.348(3)
V, Å^3	7084.0(10)	6057.5(13)
Z	4	4
ρ_{calcd}, g cm^{-3}	1.222	1.236
μ, mm^{-1}	0.883	0.76
F(000)	2772	2384
θ_{max}, deg	25.3	25.4
Collected reflections	52491	28941
Unique reflections (R_{int})	125773 (0.052)	5546 (0.046)
Observed reflections with $I > 2.0\sigma(I)$	11387	5071
GOOF	1.18	1.13
R	0.060	0.056
wR (F^2)	0.125	0.127
Largest diff. peak and hole, e Å^{-3}	0.763 and −0.617	1.042 and −0.631

obtained from the concentrated solution (10 mL) at room temperature (1.47 g, 89% based on lanthanum). m.p. 168–171°C (decomp.).

For $C_{54}H_{78}O_6Sm$ (**II**, M = 974.50)

Anal. calcd., %	C, 66.62	H, 8.08	Sm, 15.44
Found, %	C, 66.94	H, 8.65	Sm, 14.93

IR (KBr; ν_{max}, cm^{-1}): 3612 m, 3383 m, 2955 s, 2917 m, 1605 w, 1460 s, 1438 s, 1385 m, 1250 s, 1138 s, 863 w, 790 w. ^{1}H NMR (400 MHz; C_6D_6; 25°C; δ, ppm): 0.93 (H, THF), 1.44 (36H, $C(CH_3)_3$), 2.14 (12H, $ArCH_3$), 3.60 (8H, THF), 3.74 (4H, CH_2), 5.67 (1H, ArOH), 6.91 (4H, Ar), 7.05 (4H, Ar).

Synthesis of complex III. To a suspension of $LaCl_3$ (1.61 g, 6.50 mmol) in THF (50 mL) was slowly added a THF solution of LNa_2 (27.6 mL, 6.50 mmol) at room temperature. After being stirred for 24 h, colorless microcrystals of complex **III** were obtained from the 25 mL of concentrated solution at −5°C (1.45 g, 81% based on lanthanum). m.p. 157–160°C (decomp.).

For $C_{62}H_{92}O_8LaNa$ (**III**, M = 1127.31)

Anal. calcd., %	C, 66.00	H, 8.23	La, 12.32
Found, %	C, 65.87	H, 8.48	La, 12.58

IR (KBr;ν_{max}, cm^{-1}): 2949 s, 2914 m, 1605 w, 1461 s, 1434 s, 1380 m, 1253 s, 1134 s, 860 w, 790 w. ^{1}H NMR (400 MHz; C_6D_6; 25°C; δ, ppm): 1.44 (br, 8H, THF), 1.66 (m., 36 H, $C(CH_3)_3$), 2.14 (s., 12H, $ArCH_3$), 3.60 (br, 8H, THF), 3.74 (m., 4H, CH_2), 6.91 (m., 4H, Ar), 7.05 (m., 4H, Ar).

X-ray crystallography. Suitable single crystals of **II** and **III** were sealed in a thin-walled glass capillary for determining the single-crystal structures. Intensity data were collected with a Rigaku Mercury CCD area detector in ω scan mode using MoK_α radiation (λ = 0.71070 Å). The diffracted intensities were corrected for Lorentz polarization effects and empirical absorption corrections. Details of the intensity data collection and crystal data are given in Table 1. Selected

Table 2. Selected bond lengths (Å) and angles (deg) for **II** and **III***

Bond	*d*, Å	Bond	*d*, Å
		II	
Sm(1)–O(1)	2.256(3)	Sm(1)–O(2)	2.180(3)
Sm(1)–O(3)	2.265(3)	Sm(1)–O(4)	2.205(3)
Sm(1)–O(5)	2.518(3)	Sm(1)–O(6)	2.527(3)
		III	
La(1)–O(1)	2.327(3)	Na(1)–O(4)	2.288(4)
La(1)–O(2)	2.366(3)	Na(1)–O(2)	2.312(3)
La(1)–O(3)	2.623(3)		
Angle	ω, deg	Angle	ω, deg
		II	
O(2)Sm(1)O(4)	103.02(12)	O(4)Sm(1)O(6)	167.26(12)
O(2)Sm(1)O(1)	91.94(11)	O(1)Sm(1)O(6)	81.77(11)
O(4)Sm(1)O(1)	91.90(11)	O(3)Sm(1)O(6)	93.01(11)
O(2)Sm(1)O(3)	93.80(11)	O(5)Sm(1)O(6)	82.70(12)
O(4)Sm(1)O(3)	92.05(11)	O(1)Sm(1)O(5)	92.82(11)
O(1)Sm(1)O(3)	172.13(11)	O(3)Sm(1)O(5)	80.62(11)
O(2)Sm(1)O(5)	169.12(12)	O(2)Sm(1)O(6)	88.30(12)
O(4)Sm(1)O(5)	86.60(12)		
		III	
$O(1)^{\#1}La(1)O(1)$	163.05(14)	$O(2)La(1)O(3)^{\#1}$	94.63(12)
$O(1)^{\#1}La(1)O(2)$	98.22(10)	$O(3)La(1)O(3)^{\#1}$	92.46(18)
O(1)La(1)O(2)	94.88(10)	$O(4)Na(1)O(4)^{\#1}$	89.0(3)
$O(2)La(1)O(2)^{\#1}$	78.61(14)	$O(4)Na(1)O(2)^{\#1}$	122.51(13)
$O(1)^{\#1}La(1)O(3)$	77.60(11)	O(4)Na(1)O(2)	123.26(13)
O(1)La(1)O(3)	90.62(10)	$O(4)^{\#1}Na(1)O(2)$	122.51(13)
O(2)La(1)O(3)	171.82(11)	$O(2)^{\#1}Na(1)O(2)$	80.84(16)

* Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x + 1, y, -z + 3/2$.

bond lengths and angles for complexes **II** and **III** are given in Table 2.

The structures were solved by direct methods (SHELXS-97) [17] and refined by full-matrix least-squares procedures based on $|F|^2$ using SHELXL-97 [18]. The carbon atoms of the disordered solvent molecules in both of the complexes were refined isotropically, and the other non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the disordered solvent molecules were not added, and the other hydrogen atoms in these complexes were all generated geometrically, assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. All the hydrogen atoms, except those of the disordered solvent molecules, were held stationary and included in the structure factor calculation in the final stage of full-matrix least-squares refinement.

Supplementary material for structures has been deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 1500917 (**II**) and 1826699 (**III**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/).

RESULTS AND DISCUSSION

Complex $(C_5H_5)_3Sm(THF)$ was synthesized following a published procedure [19] and was used to prepare $(C_5H_5)Sm(L)(THF)_2$ (**I**) which reacted with LH_2 in a 1 : 0.5 molar ratio in toluene at 80°C for 1 day giving light yellow microcrystals **II** with high yield. However, complex **III** was obtained using a different

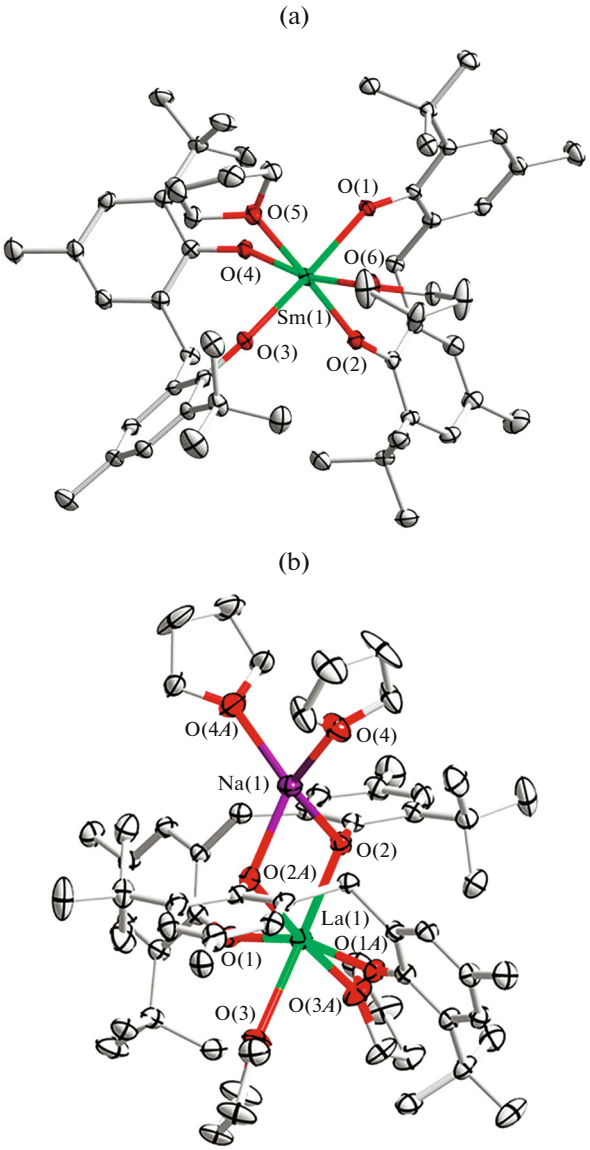


Fig. 1. General view of the molecular structures of complexes **II** (a) and **III** (b) in the crystals.

procedure, in short, using $LaCl_3$ as the precursor and reacted with LNa_2 at room temperature, colorless microcrystals **III** were also isolated in high yield as shown in Scheme 1.

Complexes **II** and **III** are sensitive to air and moisture. Complex **II** is slightly soluble in THF and hot toluene and insoluble in hexane; whereas complex **III** is soluble in THF and slightly soluble in toluene. The compositions of both complexes were established as (L)Sm(LH)-$(THF)_2$ and (L)La(LH)$(THF)_2$Na$(THF)_2$, respectively, by elemental analysis and ^{1}H NMR spectroscopy.

The coordination environment around the Sm(III) atom in **II** is shown in Fig. 1a along with the atom numbering scheme. Complex **II** has a mononuclear structure. Sm(1) is six-coordinated with distorted octahedral coordination geometry by four oxygen atoms (O(1)–O(4)) from two distinct LH_2 ligands with Sm(III)–O bond distance in the range of 2.180(3)–2.265(3) Å, and two oxygen ones (O(5), O(6)) from two different molecules THF with Sm(III)–O bond lengths of 2.518(3) and 2.527(3) Å.

The coordination environment around the La(III) atom in **III** is shown in Fig. 1b along with the atom numbering scheme. Complex **III** is six-coordinated distorted octahedral coordination geometry by four oxygen atoms from two L^{2-} groups and two oxygen atom from two THF molecules. The equatorial positions about the lanthanum centre are occupied by the terminal phenolate (O(1), O(1*A*)), one bridging phenolate (O(2*A*)) and one THF oxygen (O(3*A*)) within the octahedron. One oxygen atom from the THF (O(3)) and one oxygen from another bridging phenolate ligand (O(2)) occupy the axial positions with the O(2)LaO(3) angle to be 171.82(11)°. The overall molecular structure is similar to that of previously reported $(THF)_2Nd(L)_2Na(THF)_2$ (**IV**) which also adopts distorted octahedron [20]. The sodium centre is four-coordinated by two bridging oxygen (O(2) and O(2*A*)) from two different phenolates and two oxygen (O(2) and O(2*A*)) from THF. The average Na–O(Ar) and Na–O(THF) bond lengths are comparable with those found in **IV** [20].

It is worthy to note that the solid state structure of complex **III** is quite different from that of complex **II**. The former has a mononuclear structure, whereas the later has a dinuclear molecule. However, both complexes adopt six coordinated system. Owing to the different ionic radius (0.958 and 1.032 Å, respectively) and crystal radius (1.098 and 1.172Å, respectively) [21] of $Sm^{3+}$and La^{3+}, we speculate that the six-coordinated molecular environment is not sufficient to stabilize the La^{3+} which has the larger radius. Therefore, Na^+ and THF help the La^{3+} and $MBMPH_2$ to form a dinuclear structure.

In conclusion, two new lanthanum complexes stabilized by a carbon-bridged dianionic bis(phenolate) ligand were synthesized and fully characterized by X-ray diffraction study. The different structures of the two complexes might be related to different ionic and crystal radius.

ACKNOWLEDGMENTS

The authors thank the Education Project of Nanjing Medical University (no. YB2017050 and YB2017048) for funding.

AUTHOR CONTRIBUTIONS

K. Wang and X. M. Luo contributed equally to this work.

REFERENCES

1. Luconi, L., Lyubov, D.M., Rossin, A., et al., *Organometallics*, 2014, vol. 33, p. 7125.
2. Luo, W.L., Shi, T., Liu, S.F., et al., *Organometallics*, 2017, vol. 36, p. 1736.
3. Kourti, M.-E., Fega, E., and Pitsikalis, M., *Polym. Chem.*, 2016, vol. 7, p. 2821.
4. McKnight, A.L. and Waymouth, P.M., *Chem. Rev.*, 1998, vol. 98, p. 2587.
5. Gibson, V.C. and Spitzmesser, S.K., *Chem. Rev.*, 2003, vol. 103, p. 283.
6. Hao, Z.Q., Xu, B., Gao, W., et al., *Organometallics*, 2015, vol. 34, p. 2783.
7. Roymuhury, S.K., Chakraborty, D., and Ramkumar, V., *Dalton, Trans.*, 2015, vol. 44, p. 10352.
8. Qi, R.P., Liu, B., Xu, X.P., et al., *Dalton Trans.*, 2008, p. 5016.
9. Gonzalez-Maupoey, M., Cuenca, T., Frutos, L.M., et al., *Organometallics*, 2003, vol. 22, p. 2694.
10. Braune, W. and Okuda, J., *Angew. Chem. Int. Ed.*, 2003, vol. 42, p. 64.
11. Wu, J.C., Yu, T.L., Chen, C., et al., *Coord. Chem. Rev.*, 2006, vol. 250, p. 602.
12. Hong, K., Liang, Z.H., Ni, X.F., et al., *RSC Adv.*, 2016, vol. 6, p. 33828.
13. Zhou, Y.X., Zhao, J., Peng, L., et al., *RSC Adv.*, 2016, vol. 6, p. 22269.
14. Ikpo, N., Butt, S.M., Collins, K.L., et al., *Organometallics*, 2009, vol. 28, p. 837.
15. Dugah, D.T., Skelton, B.W., and Delbridge, E.E., *Dalton, Trans.*, 2009, p. 1436.
16. Atwood, J.L., Hunter, A.L., Wayda, A.L., et al., *Inorg. Chem.*, 1981, vol. 20, p. 4115.
17. Sheldrick, G.M., *SHELXS-97, Program for the Solution of Crystal Structures*, Göttingen: Univ. of Göttingen, 1997.
18. Sheldrick G.M., *SHELXS-97, Program for the Refinement of Crystal Structures*, Göttingen: Univ. of Göttingen, 1997.
19. Birmingham, J.M. and Wilkinson, G., *J. Am. Chem. Soc.*, 1956, vol. 78, p. 42.
20. Xu, X.P., Ma, M.T., Yao, Y.M., et al., *Eur. J. Inorg. Chem.*, 2005, p. 676.
21. Shannon, R.D., *Acta Crystallogr., Sect A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.*, 1976, vol. 32, p. 751.