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The authors congratulate Academician I.L. Eremenko on his 70th birthday

Synthesis and Molecular Structure of Binuclear *ansa*-Bis(amidinate) Ytterbium Complex $[1,3\text{-}C_6H_4\{NC(Ph)N(SiMe_3)\}_2]_3Yb_2$

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Abstract—The exchange reaction of anhydrous $YbCl_3$ with $[1,3\text{-}C_6H_4\{NC(Ph)N(SiMe_3)\}_2Li_2(THF)_2]_2$ (**I**) (4 : 3 molar ratio, THF) gave *ansa*-bis(amidinate) ytterbium complex $[1,3\text{-}C_6H_4\{NC(Ph)N(SiMe_3)\}_2]_3Yb_2$ (**II**) in which three bis(amidinate) ligands form μ-bridges between two Yb^{3+} ions. An X-ray diffraction study (CIF file CCDC no. 1964848) showed that the dimeric structure of **II** is formed upon simultaneous coordination of κ^2-N,N-chelating moieties of three ligands to two ytterbium atoms.

Keywords: lanthanides, *ansa*-bis(amidinate) ligand, ytterbium bis(amidinate), synthesis, structure

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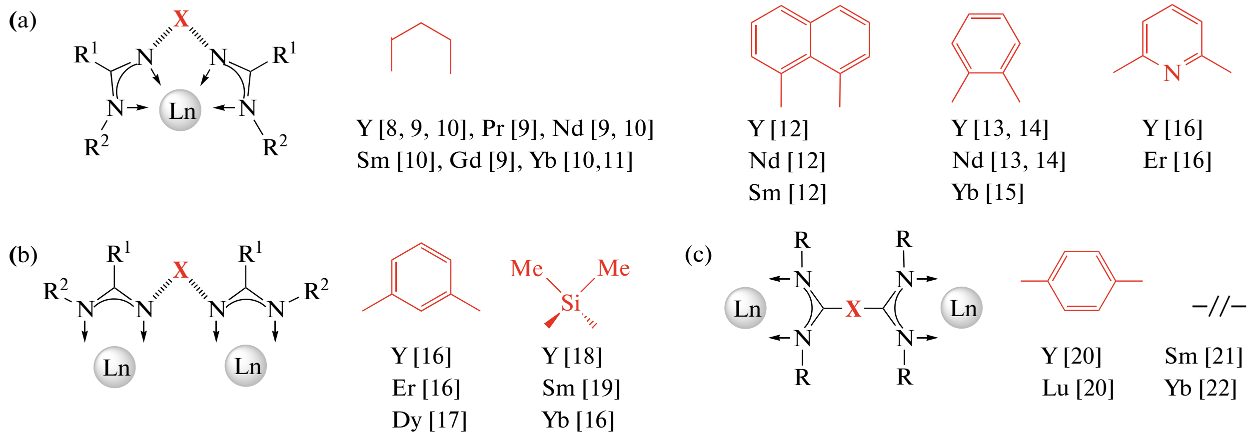
INTRODUCTION

Monoanionic amidinate ligands $[RC(NR')_2]^-$ are widely used for the synthesis of complexes of main group metals and also early and late transition metals, including lanthanides and actinides [1–3]. Owing to the conformational flexibility of ligands, diversity of ligand to metal coordination modes, and the ease of fine tuning of the steric and electronic properties by selecting substituents at nitrogen and carbon atoms, amidinate ligands are promising platforms for the synthesis of new metal complexes with tunable physicochemical properties. Dianionic *ansa*-bis(amidinate) ligands [4–7] are of interest in view of the opportunities for the design and geometry control of the metal coordination sphere in order to generate new compounds possessing luminescent and magnetic properties. Currently, there are a few known examples of using *ansa*-bis(amidinate) ligands with flexible and rigid bridging groups to prepare lanthanide complexes [8–22]. In particular, it was shown that depending on several factors (the length, nature, structure, and conformational rigidity of the group binding two amidinate moieties), both mono- and binuclear complexes can be prepared. For example, when bis(amidinate) ligand systems contain $(–CH_2–)_3$, *o*-phenylene, or $1,8\text{-}C_{10}H_8$ linker, synchronous coordination of both amidinate groups to one Ln^{3+} ion takes place (Scheme 1a), which results in the formation of mononuclear compounds [8–15]. Meanwhile, the amidinate groups of ligands containing $–SiMe_2–$ or $1,3\text{-}C_6H_4$ linker (Scheme 1b) are coordinated to different Ln^{3+} ions to give bis(amidinate)-bridged binuclear structures [16–19].



Scheme 1.

This communication reports the synthesis and structure of the complex $[1,3\text{-}C_6H_4\{NC(Ph)N(SiMe_3)\}_2]_3Yb_2$ (**II**), containing tetradentate *ansa*-bis(amidinate) ligands with the conformationally rigid *meta*-phenylene bridge.

EXPERIMENTAL

All operations on the synthesis and isolation of products were carried out under vacuum using standard Schlenck technique or a glove box with inert atmosphere (N_2). After drying with potassium hydroxide, THF was distilled from sodium benzophenone ketyl. Hexane and toluene were dried by refluxing and distillation over sodium metal. The compounds $[1,3\text{-}C_6H_4\{NC(Ph)N(SiMe_3)\}_2Li_2(THF)_2]_2$ (**I**) [13] and $YbCl_3$ [23] were synthesized according to reported procedures. *meta*-Phenylenediamine and benzonitrile were commercial chemicals (Acros). IR spectra were recorded on a Bruker-Vertex 70 instrument. Samples of compounds were prepared under dry argon as mineral oil mulls. Elemental analysis was carried out on a Perkin-Elmer Series II CHNS/O Analyser 2400. The lanthanide content was determined by complexometric titration (Trilon B) with Xylenol Orange indicator.

Synthesis of bis-ytterbium(III) tris[*N*'-1,3-phenylene-bis{*N*-trimethylsilylphenylamidinate}] (II). A suspension of **I** (1.100 g, 0.895 mmol) in THF (30 mL) was added to a suspension of $YbCl_3$ (0.333 g, 1.192 mmol) in THF (20 mL). The reaction mixture was stirred for 48 h at 25°C, and THF was removed in vacuo. The reaction product was extracted with toluene (50 mL), the solution was separated from the insoluble precipitate, and toluene was evaporated in vacuo. The product was dried for 20 min in vacuo and dissolved in a THF–hexane mixture (1 : 5). Cooling of the concentrated solution of the complex to –20°C gave light yellow crystals, which were separated from the mother liquor and dried in vacuo for 1 h to a constant weight. The yield of complex **II** was 0.863 g (80%).

For $C_{83.5}H_{107.5}N_{12}OSi_6Yb_2$

Anal. calcd., %	C, 55.41	H, 5.99	N, 9.29	Yb, 19.12
Found, %	C, 55.07	H, 5.68	N, 9.53	Yb, 19.20

Table 1. Crystallographic data and structure refinement parameters for $[1,3\text{-}C_6H_4\{NC(Ph)N(SiMe_3)\}_2]_3Yb_2 \cdot THF \cdot (C_6H_{14})_{0.25}$

Parameter	Value
M	1809.93
Space group	$P\bar{1}$
a, Å	14.8898(2)
b, Å	18.8671(2)
c, Å	32.6098(3)
α, deg	86.1870(10)
β, deg	85.9310(10)
γ, deg	78.3610(10)
V, Å^3	8937.22(18)
Z	4
Crystal size, mm	0.51 × 0.27 × 0.17
ρ(calcd.), g cm^{-3}	1.345
μ, mm^{-1}	2.209
Scanning range of θ, deg	2.94–30.034
Reflection indices hkl	$-20 \le h \le 20$, $-26 \le k \le 26$, $-45 \le l \le 45$
Number of observed/ unique reflections (R_{int})	177572/52212 (0.0624)
Number of refined parameters/constraints	2015/211
$S(F^2)$	1.019
R_1/wR_2 ($I > 2\sigma(I)$)	0.0421/0.0725
R_1/wR_2 (for all data)	0.0736/0.0803
Residual electron density (min/max), e/Å^3	–1.43/1.90

IR (ν, cm^{-1}): 1594 s, 1571 s, 1287 s, 1245 s, 1180 s, 1135 s, 1121 s, 1073 s, 1031 s, 974 s, 915 s, 892 s, 839 s, 776 s, 757 s, 698 s, 636 s, 622 s, 588 m, 518 s, 501 s, 459 s, 433 m.

X-ray diffraction study of complex **II** was carried out on a Rigaku OD Xcalibur diffractometer (ω-scan mode, $MoK_α$ radiation, $\lambda = 0.71073$ Å, $T = 100$ K). The integration of experimental sets of intensities, application of absorption corrections, and structure refinement were carried out using CrysAlisPro [24] and SHELX [25] program packages. The structure was solved by the direct method and refined by full-matrix least-squares method on F2hkl in the anisotropic approximation for nonhydrogen atoms. The hydrogen atoms in complex **II** were placed into geometrically calculated positions and refined isotropically with fixed thermal parameters $U(H)_{iso} = 1.2U(C)_{equiv}$ ($U(H)_{iso} = 1.5U(C)_{equiv}$ for methyl groups). The crystallographic data and X-ray experiment detail are summarized in Table 1; selected bond lengths and bond angles are given in Table 2. The structure is deposited with the Cambridge Crystallographic Data Centre (CCDC no. 1964848; ccdc.cam.ac.uk/getstructures).

RESULTS AND DISCUSSION

Previously, we reported the synthesis of a new *ansa*-bound bis(amidinate) ligand, $[1,3\text{-}C_6H_4\{NC(Ph)N(SiMe_3)\}_2]^{2-}$ [13], containing a conformationally rigid 1,3-C_6H_4 linker, and complexes of this ligand with erbium $[1,3\text{-}C_6H_4\{NC(Ph)N(SiMe_3)\}_2]_3Er_2(\mu\text{-}Cl)Li(THF)_3$, yttrium $[1,3\text{-}C_6H_4\{NC(Ph)N\text{-}(SiMe_3)\}_2]_3Y(THF)Y(\mu\text{-}Cl)Li(THF)_3$, and dysprosium $[1,3\text{-}C_6H_4\{NC(Ph)N(SiMe_3)\}_2]_3Dy_2$ [16, 17]. The erbium complex demonstrated field-induced slow magnetization relaxation. For the synthesis of new bis(amidinate) ytterbium chloride complexes $L_2Ln_2Cl_2$, which present potential interest as molecular magnets, we carried out the reaction of anhydrous $YbCl_3$ with $[1,3\text{-}C_6H_4\{NC(Ph)N(SiMe_3)\}_2\text{-}Li_2(THF)_2]_2$ (**I**) [13] in a 2 : 1 molar ratio in THF. However, irrespective of the molar ratio, the reaction of **I** with $YbCl_3$ affords the tris(amidinate) complex $[1,3\text{-}C_6H_4\{NC(Ph)N(SiMe_3)\}_2]_3Yb_2$ (**II**), which results from complete displacement of chloro ligands (Scheme 2).

Table 2. Selected bond lengths (d) and bond angles (ω) in complex **II**

Bond	*d*, Å	Angle	ω, deg
Yb(1)–N(1)	2.333(3)	N(1)Yb(1)N(2)	58.19(9)
Yb(1)–N(2)	2.319(2)	N(5)Yb(1)N(6)	58.16(9)
Yb(1)–N(5)	2.346(3)	N(9)Yb(1)N(10)	58.57(9)
Yb(1)–N(6)	2.303(3)	N(1)C(1)N(2)	116.6(3)
Yb(1)–N(9)	2.314(3)	N(5)C(27)N(6)	116.3(3)
Yb(1)–N(10)	2.327(3)	N(9)C(53)N(10)	116.3(3)
Yb(2)–N(3)	2.304(3)	N(3)Yb(2)N(4)	58.28(9)
Yb(2)–N(4)	2.338(3)	N(7)Yb(2)N(8)	58.51(9)
Yb(2)–N(7)	2.332(3)	N(11)Yb(2)N(12)	58.49(9)
Yb(2)–N(8)	2.318(3)	N(3)C(14)N(4)	115.9(3)
Yb(2)–N(11)	2.316(3)	N(7)C(40)N(8)	115.5(3)
Yb(2)–N(12)	2.333(3)	N(11)C(66)N(12)	116.4(3)
N(1)–C(1)	1.336(4)	C(1)Yb(1)C(27)	110.01(9)
N(2)–C(1)	1.323(4)	C(1)Yb(1)C(53)	120.51(9)
N(3)–C(14)	1.326(4)	C(27)Yb(1)C(53)	123.81(9)
N(4)–C(14)	1.342(4)	C(14)Yb(2)C(40)	125.36(9)
Si(1)–N(1)	1.737(3)	C(14)Yb(2)C(66)	122.15(9)
Si(2)–N(4)	1.730(3)	C(40)Yb(2)C(66)	108.50(9)

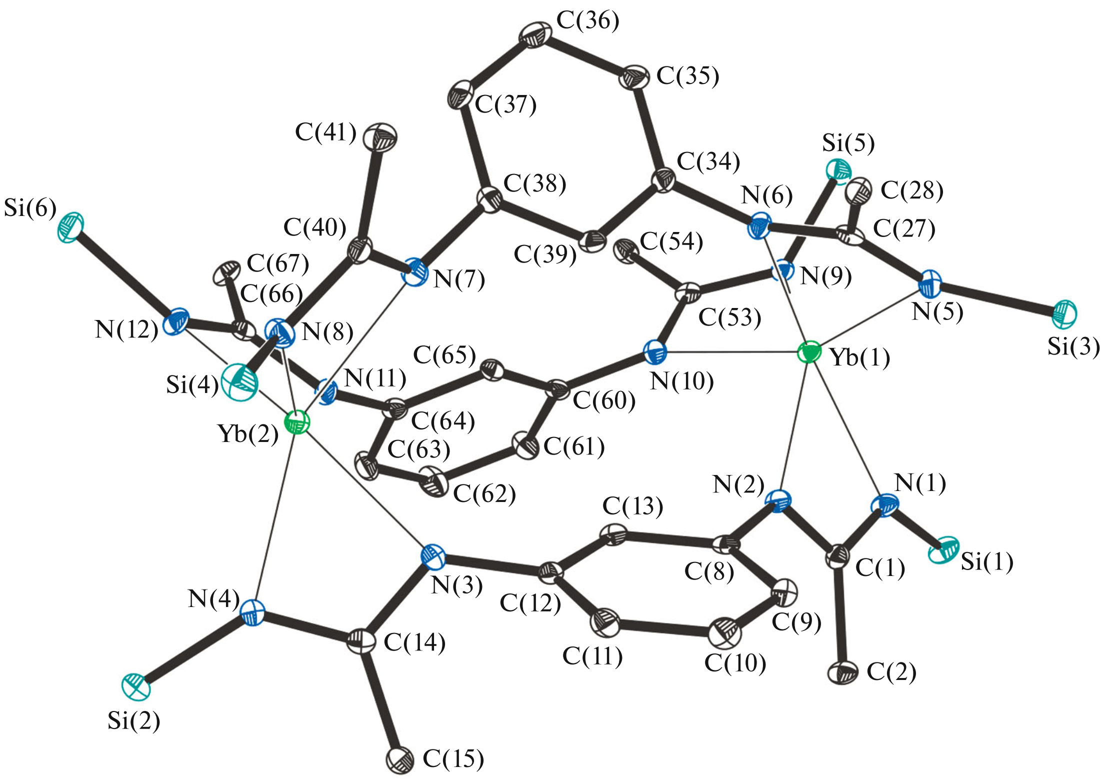
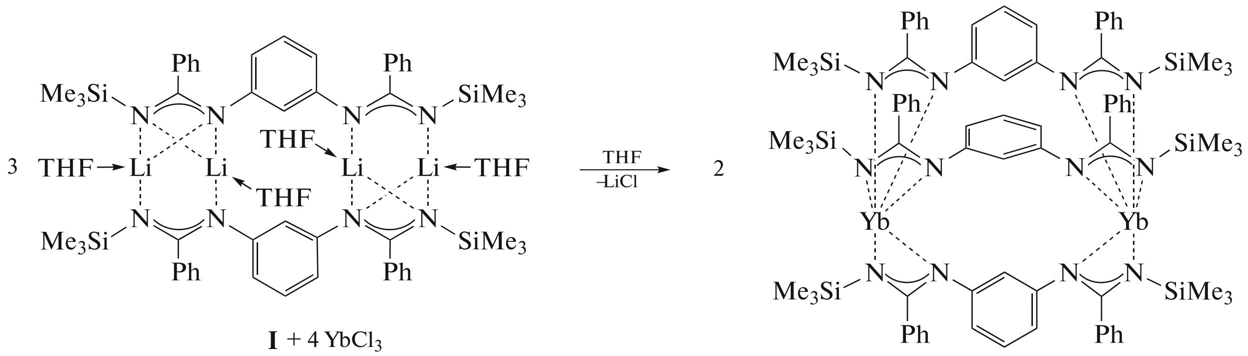


Fig. 1. Molecular structure of compound **II**. The thermal ellipsoids are drawn at 30% probability level. The hydrogen atoms, methyl groups of $SiMe_3$, and phenyl substituents are omitted for clarity.



I + 4 $YbCl_3$

II (80%)

Scheme 2.

The reaction product was extracted with toluene to separate LiCl formed in the reaction. Recrystallization from a THF–hexane mixture (1 : 5) at –20°C afforded ytterbium complex **II**, which was isolated in 39% yield as light yellow crystals, sensitive to moisture and air oxygen. The product was characterized by elemental analysis, IR spectroscopy, and X-ray diffraction. When the exchange reaction of bis(amidinate) **I** with $YbCl_3$ was carried out in THF at a 3 : 4 molar ratio, the product yield increased to 80% (Scheme 2).

The light-yellow transparent crystals of complex **II** suitable for X-ray diffraction were prepared by slow cooling of the concentrated solution of the compound in a THF–hexane mixture (1 : 5). According to X-ray diffraction data, compound **II** is a dimeric ytterbium(III) complex. The independent part of the crystal cell accommodates two molecules of the complex, two THF solvate molecules disordered over two positions, and one hexane solvate molecule located in a special position on a symmetry element. Thus, complex **II** crystallizes as the solvate [1,3-C_6H_4-

$\{NC(Ph)N(SiMe_3)\}_2]_3Yb_2 \cdot THF \cdot (C_6H_{14})_{0.25}$. The geometric parameters of crystallographically independent molecules of complex **II** are similar; therefore, the bond lengths and angles are discussed below only for one of them. The molecular structure of complex **II** is shown in Fig. 1.

The binuclear ytterbium complex **II** is formed upon coordination of the amidinate groups of *ansa*-ligands to two Yb^{3+} ions. Thus, each of the three *ansa*-bis(amidinate) ligands acts as a μ-bridge between two ytterbium cations (Fig. 1). A similar binding mode of *ansa*-bis(amidinate) ligands to lanthanide ions was previously observed in related compounds of yttrium $[Me_2Si\{NC(Ph)N(2,6\text{-}iso\text{-}Pr_2C_6H_3)\}_2]_2Y(THF)(\mu\text{-}Cl)Y(CH_2SiMe_3)$, $[Me_2Si\{NC(Ph)N(2,6\text{-}iso\text{-}Pr_2C_6H_3)\}_2Y(\mu\text{-}H)]_2$ [18], and $[1,3\text{-}C_6H_4\{NC(Ph)N(SiMe_3)\}_2]_3Y(THF)Y(\mu\text{-}Cl)Li(THF)_3$ [16]; erbium $[1,3\text{-}C_6H_4\{NC(Ph)N(SiMe_3)\}_2]_3Er_2(\mu\text{-}Cl)Li(THF)_3$ [16]; ytterbium $[Me_2Si\{NC(Ph)N(2,6\text{-}iso\text{-}Pr_2C_6H_3)\}_2]_2Yb_2Cl(\mu\text{-}Cl)_2Li(THF)_3$ [16]; and dysprosium $[1,3\text{-}C_6H_4\{NC(Ph)N(SiMe_3)\}_2]_3Dy_2$ [17]. Despite the similar values of the ionic radii of Y^{3+} (0.960 Å), Er^{3+} (0.945), Dy^{3+} (0.970) and Yb^{3+} (0.925 Å) [26] and similar isolation procedures, complex **II**, unlike $[1,3\text{-}C_6H_4\{NC(Ph)N(SiMe_3)\}_2]_3Y(THF)Y(\mu\text{-}Cl)Li(THF)_3$ or $[1,3\text{-}C_6H_4\{NC(Ph)N(SiMe_3)\}_2]_3Er_2(\mu\text{-}Cl)Li\text{-}(THF)_3$, crystallizes without $LiCl(THF)_3$. In addition, in the yttrium complex, one metal ion is coordinated by a THF molecule, whereas in a related complex, the Er^{3+} ion is linked only to three amidinate moieties [16]. Dysprosium, which has the largest ionic radius among the considered metals (C.N. 6: Dy^{3+} (0.912 Å) > Y^{3+} (0.900 Å) > Er^{3+} (0.890 Å) > Yb^{3+} (0.868 Å); C.N. 7: Dy^{3+} (0.970 Å) > Y^{3+} (0.960 Å) > Er^{3+} (0.945 Å) > Yb^{3+} (0.925 Å)) [26], forms a six-coordinate *ansa*-bis(amidinate) complex containing no coordinated THF. In complex **II**, like in the related dysprosium complex [17], each Yb^{3+} ion is coordinated to six nitrogen atoms of three amidinate moieties; thus, the formal C.N. is six. The Yb–N distances in complex **II** (2.303(3)–2.346(3) Å) differ insignificantly and are comparable with the corresponding values in related *ansa*-bis(amidinate) ytterbium complexes $[\{Me_3SiNC(Ph)N\}_2(CH_2)_3]_2Yb_2(iso\text{-}PrO)_2$ (2.304(3)–2.352(3) Å) [27] and $[\{Me_3SiNC(Ph)N\}_2(CH_2)_3]\text{-}Yb\{2,6\text{-}(tert\text{-}Bu)_2\text{-}4\text{-}MeC_6H_2\}DME$ (2.263(3)–2.586(3) Å) [10]. The C–N bond lengths in the amidinate moieties of complex **II** fit in a narrow range (1.323(4)–1.357(4) Å) and attest to delocalization of the negative charge over the NCN groups.

Thus, the binuclear ytterbium complex $[1,3\text{-}C_6H_4\{NC(Ph)N(SiMe_3)\}_2]_3Yb_2$ (**II**), containing *ansa*-bis(amidinate) ligands, was synthesized and characterized by X-ray diffraction. It is noteworthy that, irrespective of the molar ratio and the metal ionic radius, the reaction of **I** with $LnCl_3$ affords dimeric tris(amidinate) yttrium, erbium [16], dysprosium [17], or ytterbium (**II**) complex, in which two Ln^{3+} ions are connected by three bridging $[1,3\text{-}C_6H_4\{NC(Ph)N(SiMe_3)\}_2]^{2-}$ ligands.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

1. Edelmann, F.T., *Adv. Organomet. Chem.*, 2008, vol. 57, p. 183.
2. Edelmann, F.T., *Coord. Chem. Rev.*, 1994, vol. 137, p. 403.
3. Barker, J. and Kilner, M., *Coord. Chem. Rev.*, 1994, vol. 133, p. 219.
4. Whitener, G.D., Hagadorn, J.R., and Arnold, J., *J. Chem. Soc., Dalton Trans.*, 1999, p. 1249.
5. Li, J.-F., Weng, L.-H., Wei, X.-H., and Liu, D.-S., *J. Chem. Soc., Dalton Trans*, 2002, p. 1401.
6. Hill, M.S., Hitchcock, P.B., and Mansell, S.M., *Dalton Trans.*, 2006, p. 1544.
7. Bai, S.-D., Guo, J.-P., and Liu, D.-S., *Dalton Trans.*, 2006, p. 2244.
8. Wang, J., Sun, H., Yao, Y., et al., *Polyhedron*, 2008, vol. 27, p. 1977.
9. Li, W., Xue, M., Xu, F., et al., *Dalton Trans*, 2012, vol. 41, p. 8252.
10. Tu, J., Li, W., Xue, M., et al., *Dalton Trans*, 2013, vol. 42, p. 5890.
11. Wang, J., Cai, T., Yao, Y., et al., *Dalton Trans*, 2007, p. 5275.
12. Yakovenko, M.V., Cherkasov, A.V., Fukin, G.K., et al., *Eur. J. Inorg. Chem.*, 2010, p. 3290.
13. Skvortsov, G.G., Fukin, G.K., Ketkov, S.Yu., et al., *Eur. J. Inorg. Chem.*, 2013, p. 4173.
14. Tolpygin, A.O., Skvortsov, G.G., Cherkasov, A.V., et al., *Eur. J. Inorg. Chem.*, 2013, p. 6009.
15. Tolpygin, A.O., Cherkasov, A.V., Fukin, G.K., and Trifonov, A.A., *Inorg. Chem.*, 2014, vol. 53, p. 1537.
16. Skvortsov, G.G., Tolpygin, A.O., Fukin, G.K., et al., *Eur. J. Inorg. Chem.*, 2017, p. 4275.
17. Skvortsov, G.G., Cherkasov, A.V., Long, J., et al., *Mendeleev Commun.*, 2018, vol. 28, p. 521.

18. Skvortsov, G.G., Tolpyguin, A.O., Fukin, G.K., et al., *Eur. J. Inorg. Chem.*, 2010, p. 1655.
19. Pan, C.-L., Chen, W., Su, S., et al., *Dalton Trans.*, 2011, vol. 40, p. 7941.
20. Li, M., Hong, J., Chen, Z., et al., *Dalton Trans.*, 2013, vol. 42, p. 8288.
21. Deng, M., Yao, Y., Zhang, Y., and Shen, Q., *Chem. Commun.*, 2004, p. 2742.
22. Yan, L., Liu, H., Wang, J., et al., *Inorg. Chem.*, 2012, vol. 51, p. 4151.
23. Taylor, M.D. and Carter, C.P., *J. Inorg. Nucl. Chem.*, 1962, vol. 24, p. 387.
24. *CrysAlisPro*, Rigaku Oxford Diffraction, 2016.
25. Sheldrick, G.M., *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, vol. 71, p. 3.
26. Shannon, R.D., *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.*, 1976, vol. 32, p. 751.
27. Wang, J., Yao, Y., Zhang, Y., and Shen, Q., *Inorg. Chem.*, 2009, vol. 48, p. 744.

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