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Supporting Information

Synthesis of a dinuclear europium (III) complex through deprotonation and oxygen-atom transfer of trimethylamine N-oxide

Yangjuan Li,[a, b] Xiuting Chen [a] and Yu Gong *[a]

[a] Department of Radiochemistry, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai, 201800, China.

[b] School of Nuclear Science and Technology, University of Chinese Academy of Sciences, Beijing, 100049,China.

*E-mail: gongyu@sinap.ac.cn

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I. Experimental Procedures

General information

All reactions were carried out using modified Schlenk-line and Ar-atmosphere glove box (<1 ppm O_2/H_2O) techniques. Solvents were dried and degassed through a Vigor solvent purification system and stored over 4Å sieves for 24h before use. C_6D_6 and C_7D_8 were dried over Na and stored under argon atmosphere prior to use. All NMR spectra were recorded on Bruker ADVANCE-500 or AV Neo 600 spectrometers. ^{1}H and ^{13}C NMR chemical shifts (δ) are reported in ppm and were calibrated to residual solvent peaks, and ^{31}P NMR chemical shifts are relative to 85% H_3PO_4. Elemental analyses (C, H, N) were performed on a Vario EL III elemental analyser. The X-ray absorption near edge structure (XANES) spectra at the Eu L_3-edge (6977 eV) were collected at room temperature in fluorescence mode using a Lytle detector at the beamline BL14W1 of the Shanghai Synchrotron Radiation Facility (SSRF), China.[1] The powder samples were placed in the center of the polyfluortetraethylene sample holder (path length: 0.1 cm), and sealed by Kapton tape in an argon glove box. The station was operated with a Si(111) double crystal monochromator. The electron storage ring of SSRF was operated at 3.5 GeV and a current in the range of 150-210 mA. Fe metal foil with the first inflection point of Fe K-edge (7112 eV) was used to calibrate photon energy. The treatment of XANES spectra was performed using ATHENA interfaces to IFEFFIT 7.0 software.[2] Magnetization measurements of the powder samples were carried out using a Quantum Design SQUID magnetometer (type *MPMS3) in the temperature range of 1.9–300 K at a magnetic field of 0.1T. Corrections for diamagnetism of the constituting atoms were applied using Pascal's constants.[3] The effective magnetic moments were calculated from the expression $\mu_{eff} = 2.83\sqrt{\chi_m^{corr}.T(B.M.)}$.[4] $Eu[N(SiMe_3)_2]_3$ was synthesized according to literature methods.[5] Me_3NO and Me_3PO were used as purchased.

X-ray Crystallography

The intensity data of **1** were collected on Bruker D8 Venture (Mo Kα) at 193 K, and the intensity data of **2** were collected on Rigaku Synergy R (Cu Kα) at 180 K. Absorption corrections were applied by using the program CrysAlisPro (multi-scan). The crystal structures were solved by SHELXT, and nonhydrogen atoms were refined anisotropically by least-squares techniques on F^2 by SHELXL with the graphical user interfaces of OLEX2.[6] For all structures, H-atom parameters were constrained.

Synthesis of $Eu_2(OCH_2NMe_2)_2[N(SiMe_3)_2]_4$ (1)

Me_3NO (39.8 mg, 0.5 mmol) was added to a solution of $Eu[N(SiMe_3)_2]_3$ (326.1 mg, 0.5 mmol) in n-hexane (20 mL) at room temperature. The mixture was stirred for 1 h, and the color of the mixture changed to orange-yellow. After filtration, the volatile solvent in the filtrate was removed under reduced pressure. The resulting orange-yellow solid was washed by n-hexane three times and dried in vacuum. Yield: 110 mg, 39%. Anal. Calcd (%) for $C_{30}H_{88}Eu_2N_6O_2Si_8$: C, 32.95; H, 8.11; N, 7.68. Found: C, 34.26; H, 8.82; N, 7.99. The consistently high carbon content is presumably due to the high sensitivity of this compound toward moisture. ^{1}H NMR (C_6D_6, 500.1MHz, 295.6 K): δ 24.73 (s, 6H, OCH_2NMe_2), -0.02 (s, 36H, $N(SiMe_3)_2$). Signals corresponding to the OCH_2NMe_3 protons were not located between +600 and −600 ppm. ^{1}H NMR (C_7D_8, 600.1MHz, 297.4 K): δ 24.79 (s, 6H, OCH_2NMe_2), -0.07 (s, 36H, $N(SiMe_3)_2$). ^{1}H NMR (C_7D_8, 600.1MHz, 246.0 K): δ34.34 (s, 6H, OCH_2NMe_2),-0.50 (s, 36H, $N(SiMe_3)_2$). ^{13}C NMR (C_6D_6, 125.8MHz, 297.3 K): δ12.07 (OCH_2NMe_2), 1.43 ($N(SiMe_3)_2$), -14.89 (OCH_2NMe_2).

Synthesis of $Eu[N(SiMe_3)_2]_3(OPMe_3)$ (2)

The procedure for the synthesis of **2** is similar to that for the synthesis of **1**. Me_3PO (47.1 mg, 0.5 mmol) and $Eu[N(SiMe_3)_2]_3$ (321.2 mg, 0.5 mmol) gave the orange-yellow powders of **2**. Yield: 151 mg, 41%. Anal. Calcd (%) for $C_{30}H_{88}Eu_2N_6O_2Si_8$: C, 34.78; H, 8.76; N, 5.79. Found: C, 35.13; H,8.85; N, 5.38. ^{1}H NMR (C_6D_6, 600.1MHz, 303.1 K): δ 22.92 (s, 9H, $OPMe_3$), -0.59 (s, 54H, $N(SiMe_3)_2$)ppm. ^{13}C NMR (C_6D_6, 150.9MHz, 303.2 K): δ53.45 ($OPMe_3$), -0.95 ($N(SiMe_3)_2$). ^{31}P NMR (C_6D_6, 242.9 MHz, 301.1 K): δ78.51ppm.

II. Characterization

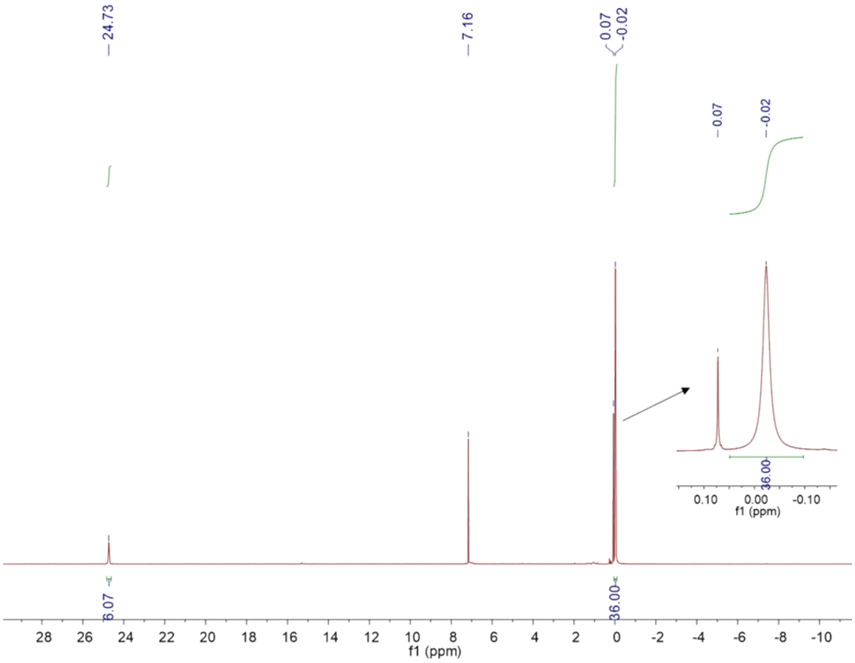

Fig. S1. ^{1}H NMR spectrum of **1** at 295.6 K in C_6D_6. The resonance at 0.07 is assignable to the hydrolysis product of **1**. The resonances of OCH_2NMe_3 protons were not observed in this spectrum.

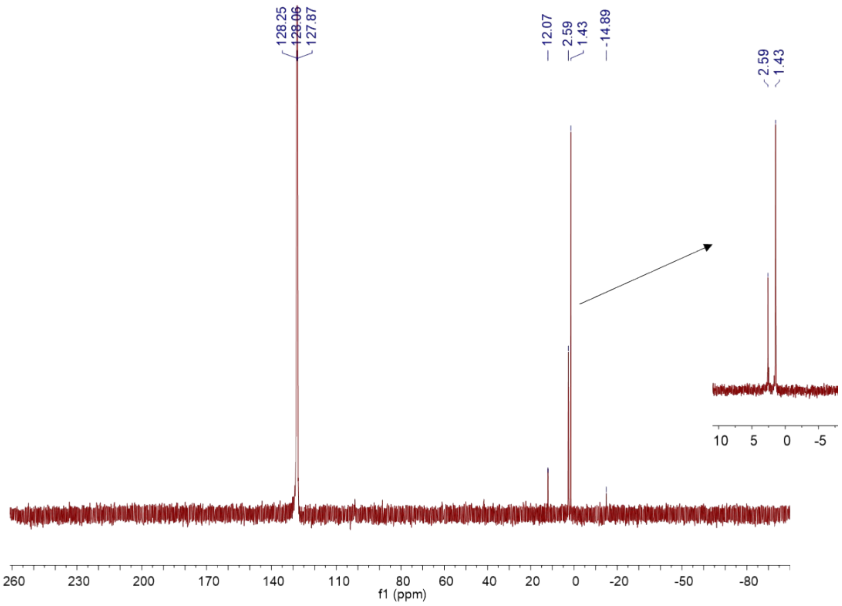

Fig. S2. ^{13}C NMR spectrum of **1** at 297.3 K in C_6D_6. The resonance at 2.59 ppm is assignable to the hydrolysis product of **1**.

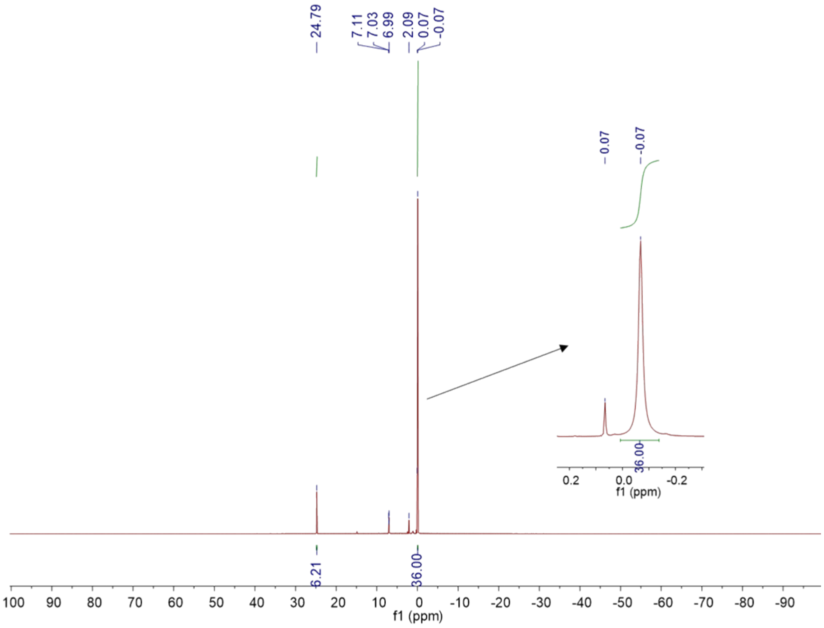

Fig. S3. ^{1}H NMR spectrum of **1** at 297.4 K in C_7D_8. The resonance at 0.07 ppm is assignable to the hydrolysis product of **1**.

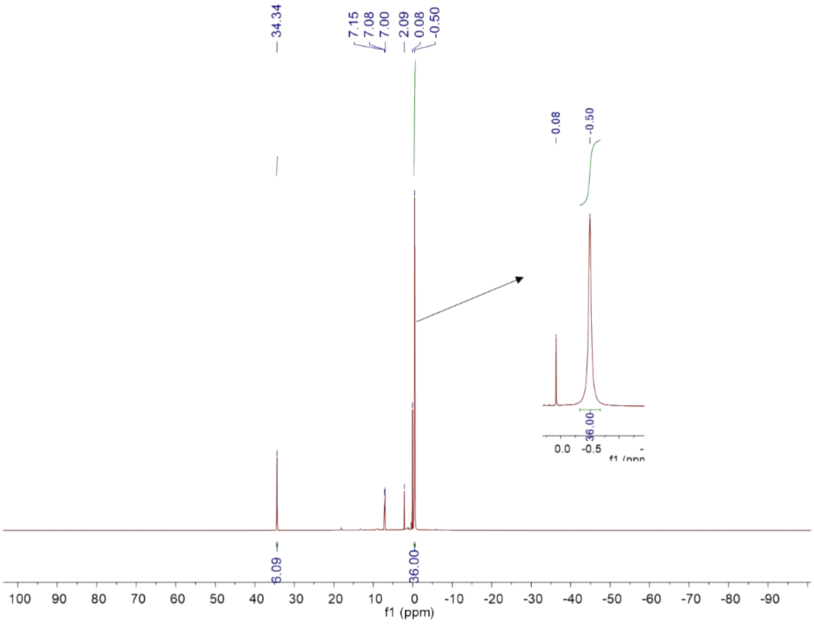

Fig. S4. ^{1}H NMR spectrum of **1** at 246.0 K in C_7D_8. The resonance at 0.08 ppm is assignable to the hydrolysis product of **1**.

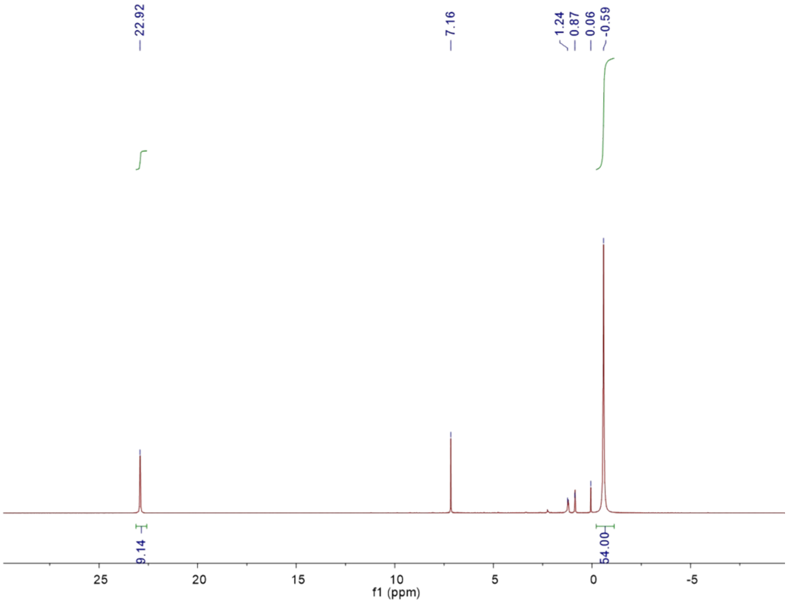

Fig. S5. ^{1}H NMR spectrum of **2** at 303.1 K in C_6D_6. The resonance at 0.06 ppm is assignable to the hydrolysis product of **2**. The resonances at 0.87 and 1.24ppm are assignable to n-hexane.

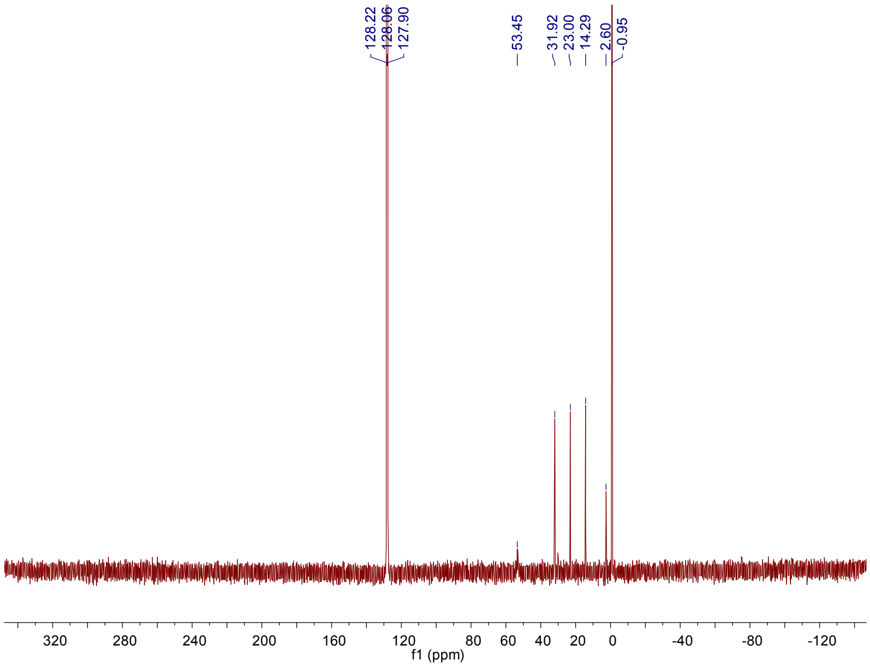

Fig. S6. ^{13}C NMR spectrum of **2** at 303.2 K in C_6D_6. The resonance at 2.60 ppm is assignable to the hydrolysis product of **2**. The resonances at 14.29, 23.00 and 31.92ppm are assigned to n-hexane.

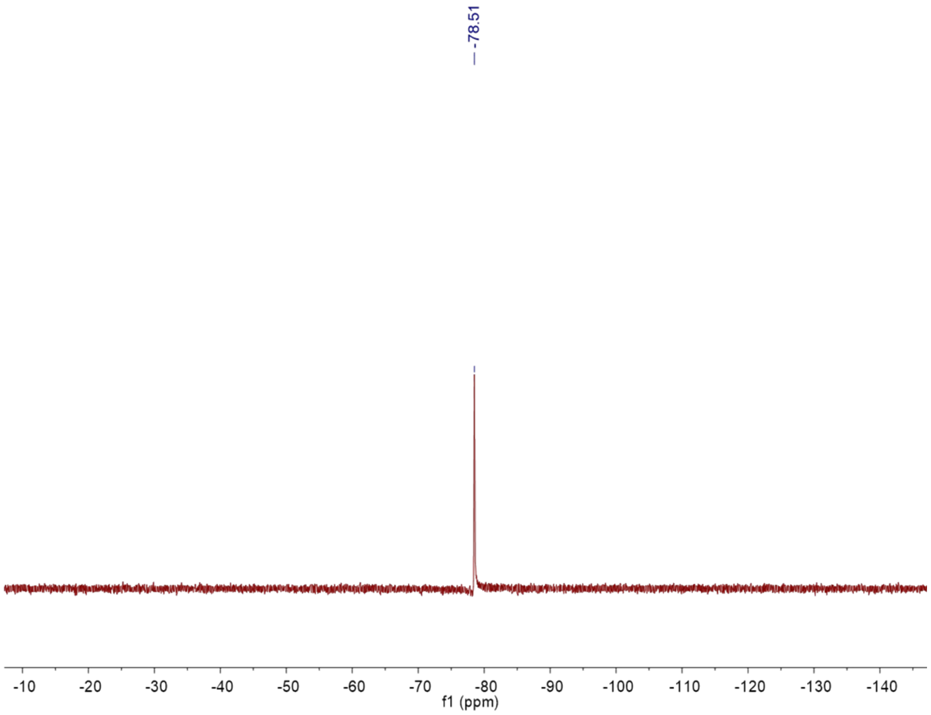

Fig. S7. ^{31}P NMR spectrum of **2** at 301.1 K in C_6D_6.

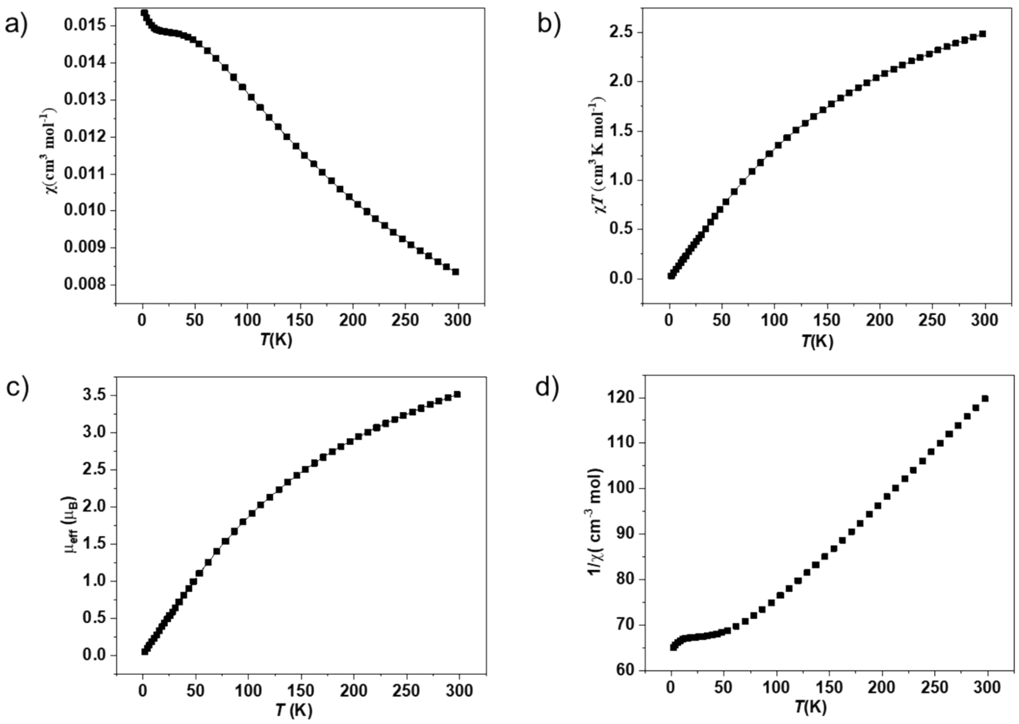

Fig. S8. Variable-temperature SQUID magnetic data for **1**: (a) χ vs. T; (b) χT vs. T; (c) μ_{eff} vs. T; (d) χ^{-1} vs. T

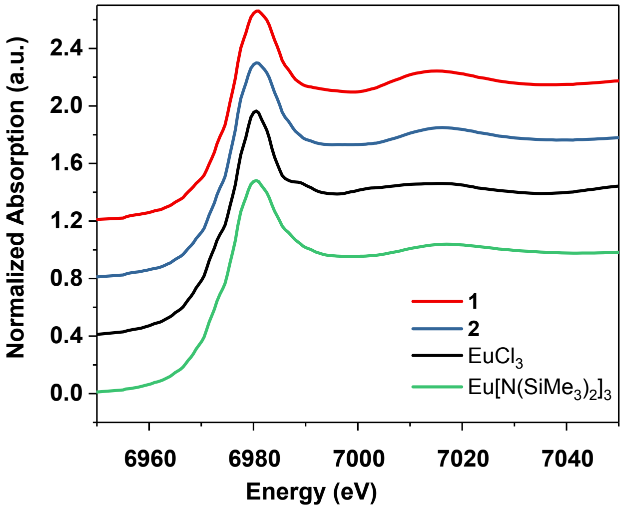

Fig. S9. Eu L$_3$-edge XANES spectra of **1**, **2**, EuCl$_3$ and Eu[N(SiMe$_3$)$_2$]$_3$

Table S1. Crystal data and structure refinements for complexes **1** and **2**

Complex	**1**	**2**
CCDC	1944303	1944305
Empirical formula	$C_{30}H_{88}Eu_2N_6O_2Si_8$	$C_{21}H_{63}EuN_3OPSi_6$
Formula weight	1093.7	241.74
Temperature/K	193(2)	180.00(10)
Crystal system	monoclinic	trigonal
Space group	P2$_1$/n	P-3

a /Å	12.1744(6)	14.69510(10)
b/Å	10.2370(5)	14.69510(10)
c/Å	20.9872(12)	11.27440(10)
α/°	90	90
β/°	91.058(2)	90
γ/°	90	120
Volume/Å^3	2615.2(2)	2108.48(3)
Z	2	6
ρ_{calc}g/cm^3	1.389	1.142
μ/mm^{-1}	2.59	12.753
F(000)	1128	760
θ range/deg	5.528 to 51.986	10.482 to 133.052
Index ranges	$-14 \leq h \leq 15$ $-12 \leq k \leq 12$ $-25 \leq l \leq 25$	$-17 \leq h \leq 13$ $-15 \leq k \leq 17$ $-10 \leq l \leq 13$
Reflections collected	25544	12326
Independent reflections	5130 R_{int} = 0.0404 R_{sigma} = 0.0297	2469 R_{int} = 0.0273 R_{sigma} = 0.0189
Completeness	100%	100%
Data/restraints/parameters	5130/0/240	2469/0/107
Goodness-of-fit on F^2	1.079	1.063
Final R indexes [I>=2σ (I)]	R_1 = 0.0197 wR_2 = 0.0445	R_1 = 0.0307 wR_2 = 0.0790
Final R indexes [all data]	R_1 = 0.0234 wR_2 = 0.0465	R_1 = 0.0353 wR_2 = 0.0806
Largest diff. peak/hole / e Å^{-3}	0.52/-0.56	0.40/-0.76

III. References

1. H. S. Yu, X. J. Wei, J. Li, S. Q. Gu, S. Zhang, L. H. Wang, J. Y. Ma, L. N. Li, Q. Gao, R. Si, F. F. Sun, Y. Wang, F. Song, H. J. Xu, X. H. Yu, Y. Zou, J. Q. Wang, Z. Jiang and Y. Y. Huang, *Nucl.Sci.Technol.*, 2015, **26**, No. 050102.
2. (a)M. Newville, *J. Synchrotron Radiat.*, 2001, **8**, 96; (b)B. Ravel and M. Newville, *J. Synchrotron Radiat.*, 2005, **12**, 537.
3. G. A. Bain and J. F. Berry, *J. Chem. Educ.*, 2008, **85**, 532.
4. I. Pospieszna-Markiewicz, W. Radecka-Paryzek, M. Kubicki, M. Korabik and Z. Hnatejko, *Polyhedron*, 2015, **97**, 167.
5. D. C. Bradley, Ghotra,J. S. , Hart,F. A., *J. Chem. Soc., Dalton Trans.*, 1973, 1021.
6. (a)O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339; (b)G. Sheldrick, *Acta Crystallogr. Section A*, 2015, **71**, 3; (c)G. M. Sheldrick, *Acta Crystallogr. Section C*, 2015, **71**, 3.