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Two Sr^{II} coordination compounds based on tetrazole-carboxylate ligands

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Abstract: Two novel coordination compounds, $[Sr(atzp)_2(H_2O)_3] \cdot CH_2OH$ (1) and $[Sr(dtzpha)(H_2O)_3] \cdot 4H_2O$ (2) [Hatzp=5-aminotetrazole-1-propionic acid, H,dtzpha= 1,3-di(tetrazol-5-vl)benzene-N2,N2'-diacetic acid)], have been generated by using 5-aminotetrazole-1-propionic 1,3-di(tetrazol-5-yl)benzene-N2,N2'-diacetic acid acid to react with strontium salts, respectively. X-ray diffraction analysis reveals that carboxylic groups of two ligands show the same coordination mode (the μ_{113} -COO coordination mode), compound 1 displays a 1D structure while compound 2 shows a 2D structure, which implies the influence of the number of the carboxylic acid groups. Luminescence properties of 1 and 2 were investigated at room temperature in the solid state.

Keywords: crystal structure; Hatzp; H₂dtzpha; Sr(II); tetrazole-carboxylate ligands.

Introduction

It is generally acknowledged that there are many factors, such as metal-ligand ratio, solvents, temperature, organic ligands and so on, having an inevitable impact on the structures of the targeted molecules (for reviews, see Dong et al., 2008; Li et al., 2014, 2015; Zou et al., 2014a,b). For these influencing factors, organic ligands, in particular, play a very important role in the novel structures of coordination compounds. Indeed, in multitudinous organic ligands, tetrazole-carboxylate

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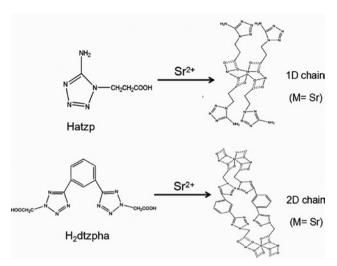
ligands, in which carboxylate oxygen atoms and tetrazolyl nitrogen atoms both have good coordination capacities, have been widely employed because, in the self-assembling process, the shapes of the tetrazole-carboxylate ligands are very important in the control of the frameworks. Therefore, it is possible to generate the targeted architecture through the choice of tetrazole-carboxylate ligands.

Based on the above facts, we have successfully designed two novel tetrazole-carboxylate ligands, 5-aminotetrazole-1-propionic acid and 1,3-di(tetrazol-5-yl)benzene-N2,N2'-diacetic acid to construct novel coordination compounds with fascinating structures. comparing 5-aminotetrazole-1-propionic with 1,3-di(tetrazol-5-yl)benzene-N2,N2'-diacetic 1,3-di(tetrazol-5-yl)benzene-N2,N2'-diacetic acid has more carboxylate group, which enables it to increase the connectivity of the network and thus to promote an increase of the dimensionality. So, in our study, 5-aminotetrazole-1-propionic acid and 1,3-di(tetrazol-5-yl)benzene-N2,N2'diacetic acid have been chosen to react with strontium salts, thus obtaining [Sr(atzp)₂(H₂O)₃]·CH₂OH (1) and $[Sr(dtzpha)(H_2O)_3]\cdot 4H_2O$ (2) (Scheme 1). The structures and the luminescence properties of the compounds 1 and 2 also have been reported.

Results and discussion

Synthesis consideration and general characterizations of 1 and 2

Compound 1 is stable towards air while compound 2 is not. All general characterizations are carried out with crystal samples. For 1–2, strong absorptions at 1660–1621 cm $^{-1}$ correspond to ν (COO) vibration of the carboxylate group. The formation of the tetrazole group is supported by the emergence of the peak from 1400 to 1549 cm $^{-1}$ (Perkovic, 2000). In addition, the strong and broad band centered at 3130, 3392, 3433 cm $^{-1}$ for the coordination compounds are attributable to the O-H stretching vibration of water, including water for both compounds 1 and 2, and methanol just for compound 2.



Scheme 1: The synthesis procedure caused by the differences in the number of carboxylic acid groups of the ligands.

Crystal structure of [Sr(atzp),(H,O),]·CH,OH (1)

Single crystal X-ray diffraction reveals that compound 1 crystallizes in triclinic space group $P\overline{1}$. As shown in Figure 1, each Sr(II) is eight-coordinated by six carboxylate-O atoms (O1, O1A, O2, O3, O3B, O5) from four 5-aminotetrazole-1-propionic acid ligands, two O atoms (O5, O6) from two water molecules, forming a distorted square-antiprism structure. In 1, two adjacent Sr(II) ions are doubly bridged by two carboxylate groups from two 5-aminotetrazole-1-propionic acid ligands in a $\mu_{1.1.3}$ -COO

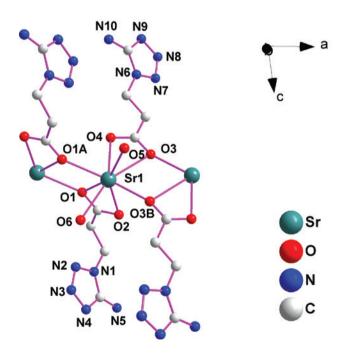


Figure 1: The coordination environment of Sr(II) in **1**. Hydrogen atoms are omitted for clarity.

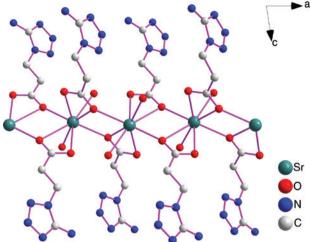


Figure 2: The 1D chain structure of ${\bf 1}$ which is extending along the a axis.

Hydrogen atoms are omitted for clarity.

coordination mode, forming a 1D chain extending along the a axis with the Sr···Sr distances of 4.1536 and 4.1857 Å and the Sr···Sr···Sr angle of 147.352° (Figure 2). In **1**, many hydrogen bonds link the layers into a 3D supramolecular framework. Tetrazole ring provides an intralayer hydrogen bond $[N(5)\cdots O(7), 2.983(17) \text{ Å}]$ to O of the uncoordinated water and amino provides an intralayer hydrogen bond $[N(10)\cdots N(3), 3.014(6) \text{ Å}]$ to N of the tetrazole ring to consolidate the layer structure. Another hydrogen bond connects the layers through water via hydrogen bonds $[O(5)\cdots O(2), 2.898(5) \text{ Å}]$ to O of the carboxylate (Figure 3).

Crystal structure of [Sr(dtzpha) (H,O),]·4H,O (2)

Compound **2** crystallizes in triclinic space group $P\overline{1}$. As shown in Figure 4, each Sr(II) is nine-coordinated by

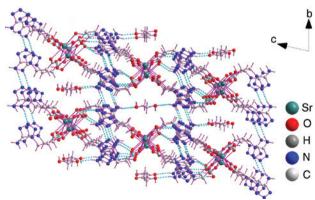


Figure 3: View of 1, showing hydrogen-bonding interactions.

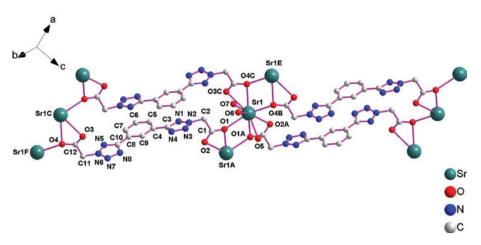


Figure 4: The coordination environment of Sr(II) in 2. Hydrogen atoms are omitted for clarity.

six carboxylate-O atoms (O1, O1A, O2A, O3C, O4B, O4C) from four 1,3-di(tetrazol-5-yl)benzene-N2,N2'-diacetic acid ligands, three water-O atoms (O5, O6, O7), forming a monocapped square-antiprism coordination geometry. In 2, both the carboxylic acids of the 1,3-di(tetrazol-5-yl) benzene-N2,N2'-diacetic acid ligand coordinate to four Sr(II) ions in a $\mu_{1.1.3}$ -COO coordination mode, thereby forming a 2D layer structure (Figure 5A). The structure

can be simplified as a (4,4) rhomboidal grid topology with diagonal lengths of 16.8821 and 17.9619 Å (Figure 5B), and many hydrogen bonds link the layers into a 3D supramolecular framework. Uncoordinated water provides an intralayer hydrogen bond [O(7)···N(1), 3.33(2) Å] to N of the tetrazole ring and coordinated water provides an intralayer hydrogen bond [O(5)···N(8), 3.004(9) Å] to N of the benzene ring to consolidate the layer structure. Another

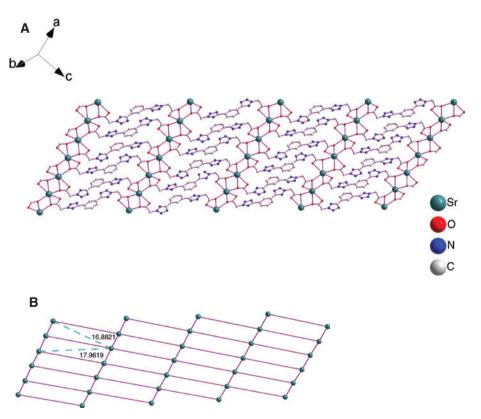


Figure 5: (A) The 2D chain structure of 2. Hydrogen atoms are omitted for clarity. (B) The (4,4) topology of compound 2.

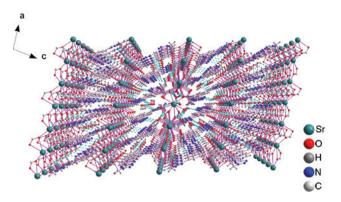


Figure 6: View of 2, showing hydrogen-bonding interactions.

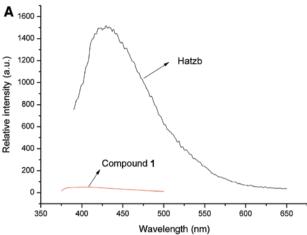
hydrogen bond connects the layers through water via hydrogen bonds $[O(5)\cdots O(1), 3.174(11) \text{ Å}]$ to O of the carboxylate (Figure 6).

Luminescent properties

The luminescence properties of 1-2 and the free ligands were investigated in the solid state at room temperature. As shown in Figure 7, the free ligands, 5-aminotetrazole-1-propionic acid and 1,3-di(tetrazol-5-vl)benzene-N2,N2'-diacetic acid exhibit maximum emissions at 433 and 360 nm upon excitations at 371 and 315 nm, respectively. Compounds 1 and 2 exhibit photoluminescence with maximum emissions at 405 and 409 nm upon excitations at 357 and 336 nm, respectively. Hence fluorescent emissions could be tentatively assigned to the intraligand fluorescent emissions. Compared to the corresponding ligands, a blue shift of 28 nm for compound 1 and a red shift of 49 nm for compound 2 have been observed, respectively, which implies that the shifts may be attributed to the coordination effects of Sr^{II} with the two ligands (Zou et al., 2014a,b). Generally, the intraligand fluorescence emission wavelength is determined by the energy gap between the π and π^* molecular orbitals of the free ligand, which is related to the extent of π conjugation (Li et al., 2011; Wu et al., 2015; Zou et al., 2015).

Conclusion

In this study, under the same experimental conditions, the reaction of 5-aminotetrazole-1-propionic acid and 1,3-di(tetrazol-5-yl)benzene-N2,N2'-diacetic acid with strontium salts, respectively gives two compounds



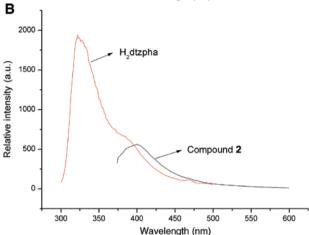


Figure 7: (A) Emission spectra of compound 1 and 5-aminotetrazole-1-propionic acid in the solid state at room temperature (for 5-aminotetrazole-1-propionic acid $\lambda_{\rm ex}=371$ nm, for $1\lambda_{\rm ex}=357$ nm). (B) Emission spectra of compound 2 and 1,3-di(tetrazol-5-yl) benzene-N2,N2′-diacetic acid in the solid state at room temperature [for 1,3-di(tetrazol-5-yl)benzene-N2,N2′-diacetic acid $\lambda_{\rm ex}=315$ nm, for $2\lambda_{\rm ex}=336$ nm].

with distinctly different structures. For **1**, the bidentate 5-aminotetrazole-1-propionic acid ligand is capable of coordinating the neighboring Sr(II) ions through two carboxylate-O atoms in a $\mu_{1,1,3}$ -COO coordination mode to form a 1D chain. However, in **2**, the 1,3-di(tetrazol-5-yl)benzene-N2,N2'-diacetic acid ligand acts as a hexadentate ligand to coordinate four Sr(II) ions via four carboxylate-O atoms in a $\mu_{1,1,3}$ -COO coordination mode to form a 2D structure, demonstrating that the differences between the coordination structures are reflected in the number of carboxylic acid groups. The photoluminescence measurements show **1** and **2** exhibit strong photoluminescence at room temperature in the solid state.

Inspired by these observations, the approach that changes the shape of tetrazole-carboxylate ligands via controlling the number of carboxylic acid is expected to be effective for further construction of novel coordination frameworks.

Experimental section

Materials and instrumentation

General chemicals were commercially available reagents of analytical grade and were used without further purification. The elemental analyses for C, H, and N were performed on a PE-2400 Microanalyzer (PerkinElmer, USA). All NMR spectra were taken on a Bruker AVANCEIII-HD-400 MHz spectrometer (Bruker, Switzerland). The IR spectra were recorded on a thermo NICOLET-380 instrument (Thermo Fisher Scientific, USA) as KBr disk (4000-400 cm⁻¹). Photoluminescent spectra were performed on a Hitachi F-4600 spectrofluorometer (Hitachi, Japan). Single crystal X-ray diffraction was carried out by a Rigaku SCXmini CCD diffractometer.

Synthesis of 5-aminotetrazole-1-propionic acid (Hatzp) and 1,3-di(tetrazol-5-yl)benzene-N2,N2'-diacetic acid (Hadtzpha)

5-Aminotetrazole and 1,3-di(tetrazol-5-yl)benzene were prepared by [2+3] cycloaddition reactions, by treating dicyandiamide or 1,3-dicyanobenzene with NaN, in toluene in the presence of triethylammonium chloride. 5-Aminotetrazole-1-propionic acid (Hatzp) was prepared by the reaction of 5-aminotetrazole with 3-bromopropionic acid in sodium hydroxide solution, while the reaction of 1,3-di(tetrazol-5-yl)benzene with chloroacetic acid in sodium hydroxide solution gave mostly 1,3-di(tetrazol-5-yl)benzene-N2.N2'-diacetic acid(H.dtzpha) products (Shen et al., 2015, 2016; Wang et al., 2016; Yang et al., 2016). For Hatzp: anal. calcd for C₁₂H₁₀N₂O₄: C, 43.64; H, 3.05; N, 33.93%. Found: C, 43.89; H, 3.11; N, 34.33%. IR (KBr, cm⁻¹): 3337(m); 3160(m); 1721(s); 1670(s); 1415(m); 1596(w); 1225(w); 1472(w); 1372(s); 1257(m); 1096(m); 1063(m); 788(w); 695(m). ¹HNMR (DMSO, δppm): 4.71, 5.82(-CH.); 9.52(-NH.); 11.49(-COOH). ¹³CNMR (DMSO, δppm): 30.50(-CH₂-); 56.85(-N-CH₂-); 150.52(C=N); 173.88(C=O). For H₂dtzpha: anal. calcd for $C_oH_{10}N_oO_a$: C, 34.05; H, 3.57; N, 39.70%. Found: C, 34.33; H, 3.60; N, 39.56%. IR (KBr, cm⁻¹): 3263(s); 3108(m); 2990(m); 1719(s); 1550(s); 1423(w); 1236(w); 1045(w); 1457(w); 817(w); 744(w); 664(w); 532(w). ¹HNMR (DMSO, δppm): 5.28(-N-CH₂-); 7.70, 8.07, 8.26(-C_εH₆); 11.98(-COOH). ¹³CNMR (DMSO, δppm): 49.98(-N-CH₂-); 119.12, 129.68, 130.36, 134.36(C=C); 166.13(C=N); 167.21(-COOH).

Synthesis of [Sr(atzp),(H,O),]-CH,OH (1)

5-Aminotetrazole-1-propionic acid (Hatzp) (0.0114 g, 0.1 mmol) was dissolved in 0.5 mL distilled water, and the pH value was adjusted to 6 with KOH (0.2 mol/L). SrCl₂·6H₂O (0.0267 g, 0.1 mmol) and methanol (3 mL) were added to the solution. The mixture was heated at 60°C in a thermostat water bath for 1 h, then cooled to the room temperature, and filtered; the block crystals 1 was obtained in mother liquors. For 1, yield: 54% based on Sr²⁺ consumed. Anal. calcd for C₀H₁₀N₁₀O₂Sr:

Table 1: Selected crystallographic data and structure refinement for 1–2.

| Compound | 1 | 2 |
|---|------------------------|--|
| Empirical formula | $C_9H_{20}N_{10}O_7Sr$ | C ₁₂ H ₁₂ N ₈ O ₆ Sr·4(H ₂ O) |
| Formula mass | 467.97 | 523.98 |
| Crystal system | Triclinic | Triclinic |
| Space group | $P\overline{1}$ | $P\overline{1}$ |
| a (Å) | 8.0028(16) | 9.3358(10) |
| <i>b</i> (Å) | 10.832(2) | 10.5581(12) |
| c (Å) | 11.822(2) | 11.4433(13) |
| α (°) | 75.35(3) | 100.1500(15) |
| β (°) | 79.16(3) | 95.6730(14) |
| γ (°) | 78.35(3) | 106.2030(13) |
| V (ų) | 960.9(3) | 1053.0(2) |
| Z | 2 | 2 |
| T/K | 291(2) | 296(2) |
| $D_{\rm calcd}$ (g.cm ⁻³) | 1.617 | 1.653 |
| μ (mm ⁻¹) | 2.860 | 2.627 |
| Reflections collected | 10073 | 6163 |
| Unique reflections (R _{int}) | 4383 (0.0383) | 3565 (0.0155) |
| No. observations $[l>2\sigma(l)]$ | 3764 | 3177 |
| No. variables | 235 | 266 |
| R_{1}^{a} , wR_{2}^{b} [$l > 2\sigma(l)$] | 0.0522, 0.1443 | 0.0617, 0.1844 |
| GOF ^c | 1.069 | 0.836 |
| $\Delta/\rho_{\rm max}$ (e/Å ³) | 1.060 | 1.773 |
| $\Delta/\rho_{\min}(e/Å^3)$ | -0.875 | -0.825 |

 $^{{}^{}a}R = \Sigma ||F_{o}| - |F_{c}|/\Sigma |F_{o}|$. ${}^{b}Rw = [\Sigma w(F_{o}^{2} - F_{c}^{2})^{2}/\Sigma w(F_{o}^{2})^{2}]^{1/2}$. ${}^{c}GOF = \{\Sigma [w((F_{o}^{2} - F_{c}^{2})^{2})/(n-p)]\}^{1/2}$, where n, number of reflections; p, total numbers of parameters refined.

C, 23.10; H, 4.31; N, 29.93%. Found: C, 23.33; H, 4.42; N, 30.34%. IR (KBr, cm⁻¹): 3392(s), 1653(m), 1638(m), 1549(s), 1493(w), 1443(m), 1269(w), 1126(w), 1087(w), 956(w), 674(m).

Synthesis of [Sr(dtzpha)(H,O),].4H,O (2)

1,3-Di(tetrazol-5-yl)benzene-N2,N2'-diacetic acid (H,dtzpha) (0.0332 g, 0.1 mmol) was dissolved in 1 mL distilled water, and the pH value

was adjusted to 6 with KOH (0.2 mol/L). SrCl₂·6H₂O (0.0267 g, 0.1 mmol) and methanol (3 mL) were added to the solution. The mixture was heated at 60°C in a thermostat water bath for 1 h, then cooled to the room temperature, and filtered; the block crystals 2 were obtained in mother liquors. For 2, yield: 40% based on Sr^{2+} consumed. Anal. calcd for C₁₂H₂₀N₈O₁₀Sr: C, 27.51; H, 3.85; N, 21.39%. Found: C, 27.73; H, 3.78; N, 21.59%. IR (KBr, cm⁻¹): 3433(s), 3130(s), 1660(m), 1621(s), 1453(m), 1433(m), 1400(s), 1205(w), 1139(w), 1069(m), 951(w), 862(w), 834(w), 814(w), 742(m), 680(w).

Table 2: Selected bond distances and angles for compounds 1 and 2 ($\mathring{A}/^{\circ}$).

| Compound 1 | | | |
|---------------------------------------|--------------------------|---------------------------------------|--------------------------|
| Sr(1)-0(3B) | 2.505(3) | Sr (1)-O(1A) | 2.507(3) |
| Sr(1)-0(6) | 2.554(3) | Sr (1)-O(4) | 2.579(3) |
| Sr(1)-O(5) | 2.632(3) | Sr(1)-O(2) | 2.677(3) |
| Sr(1)-O(1) | 2.690(3) | Sr (1)-0(3) | 2.756(3) |
| O(3B)-Sr(1)-O(1A) | 150.85(11) | O(3B)-Sr(1)-O(6) | 87.74(11) |
| O(1A)-Sr(1)-O(6) | 77.95(11) | O(3B)-Sr(1)-O(4) | 123.30(10) |
| O(1A)-Sr(1)-O(4) | 76.09(11) | 0(6)-Sr(1)-0(4) | 148.45(11) |
| O(3)-Sr(1)-O(5) | 72.05(11) | O(1A)-Sr(1)-O(5) | 88.89(10) |
| O(6)-Sr(1)-O(5) | 109.68(13) | O(4)-Sr(1)-O(5) | 87.50(13) |
| O(3)-Sr(1)-O(2) | 81.59(10) | O(1A)-Sr(1)-O(2) | 120.09(10) |
| O(6)-Sr(1)-O(2) | 80.58(12) | O(4)-Sr(1)-O(2) | 97.25(13) |
| O(5)-Sr(1)-O(2) | 150.96(10) | O(3B)-Sr(1)-O(1) | 130.07(10) |
| O(1A)-Sr(1)-O(1) | 72.74(11) | 0(6)-Sr(1)-0(1) | 80.33(11) |
| O(4)-Sr(1)-O(1) | 75.08(12) | 0(5)-Sr(1)-0(1) | 157.09(10) |
| O(2)-Sr(1)-O(1) | 48.74(9) | O(3B)-Sr(1)-O(3) | 75.84(11) |
| O(1A)-Sr(1)-O(3) | 123.87(10) | 0(6)-Sr(1)-0(3) | 156.66(12) |
| O(4)-Sr(1)-O(3) | 48.56(9) | 0(5)-Sr(1)-O(3) | 81.23(11) |
| O(2)-Sr(1)-O(3) | 80.69(10) | O(1)-Sr(1)-O(3) | 97.48(10) |
| | , | | , |
| Compound 2 | | - () - (-) | |
| Sr(1)-O(1) | 2.703(5) | Sr(1)-O(4B) | 2.718(5) |
| Sr(1)-O(6) | 2.756(7) | Sr(1)-O(5) | 2.826(7) |
| Sr(1)-O(7) | 2.928(6) | Sr(1)-O(4C) | 2.906(5) |
| Sr(1)-0(3C) | 2.908(5) | Sr(1)-O(1A) | 2.910(5) |
| Sr(1)-O(2A) | 2.934(6) | | |
| O(1)-Sr(1)-O(4B) | 152.52(18) | 0(1)-Sr(1)-0(6) | 76.22(17) |
| O(4B)-Sr(1)-O(6) | 83.49(17) | 0(1)-Sr(1)-O(5) | 79.52(18) |
| O(4B)-Sr(1)-O(5) | 77.46(15) | 0(6)-Sr(1)-O(5) | 75.1(2) |
| 0(3C)-Sr(1)-0(7) | 60.43(16) | 0(4C)-Sr(1)-O(7) | 89.07(15) |
| 0(1A)-Sr(1)-0(7) | 73.75(17) | O(2A)-Sr(1)-O(7) | 84.63(17) |
| 0(1)-Sr(1)-0(4C) | 119.10(13) | O(4B)-Sr(1)-O(4C) | 68.24(14) |
| 0(6)-Sr(1)-0(4C) | 68.29(16) | O(5)-Sr(1)-O(4C) | 131.65(16) |
| 0(3C)-Sr(1)-0(2A) | 140.89(15) | 0(1)-Sr(1)-0(3C) | 77.85(14) |
| 0(4B)-Sr(1)-0(3C) | 112.79(12) | O(6)-Sr(1)-O(3C) | 70.71(19) |
| 0(5)-Sr(1)-0(3C) | 142.5(2) | O(4C)-Sr(1)-O(2A) | 125.41(12) |
| 0(4C)-Sr(1)-0(3C) | 44.67(12) | O(1)-Sr(1)-O(1A) | 66.83(17) |
| O(4B)-Sr(1)-O(1A) O(5)-Sr(1)-O(1A) | 116.25(13) 66.91(18) | O(6)-Sr(1)-O(1A) O(1A)-Sr(1)-O(2A) | 130.45(17) |
| | | | 44.35(13) |
| O(4C)-Sr(1)- $O(1A)$ | 159.98(18) 111.17(13) | 0(3C)-Sr(1)-O(1A) | 127.93(13) 77.27(13) |
| O(1A)-Sr(1)-O(2A) O(6)-Sr(1)-O(2A) | 111.17(13) 147.7(2) | O(4B)-Sr(1)-O(2A) O(5)-Sr(1)-O(2A) | 77.27(13) 75.6(2) |
| | | | |
| O(1)-Sr(1)-O(7) O(6)-Sr(1)-O(7) | 74.63(17) 126.9(2) | O(4B)-Sr(1)-O(7) O(5)-Sr(1)-O(7) | 132.84(15) 138.95(17) |
| U(0)-31(1)-U(/) | 120.9(2) | U(5)-31(1)-U(7) | 138.95(1/) |

 $Symmetry\ code:\ For\ 1:\ A:\ 1-x,\ 1-y,\ -z;\ B:\ 2-x,\ 1-y,\ -z.\ For\ 2:\ A:\ 2-x,\ -y,\ 2-z;\ B:\ 1+x,\ -1+y,\ 1+z;\ C:\ 2-x,\ 1-y,\ 1-z;\ D:\ 2-x,\ -y,\ 1-z.$

X-ray crystallography

Suitable single crystals of compounds 1-2 were mounted on a Rigaku SCXmini CCD diffractometer equipped with a graphite-monochromated Mo-K α radiation (λ = 0.071073 Å) at 291 K. All absorption corrections were performed using the Crystal-Clear programs. The crystal structures of 1–2 were solved by direct methods and refined on F^2 by full-matrix least-squares using anisotropic displacement parameters for all nonhydrogen atoms (Sheldrick, 1997). For 1-2, more relevant refinement data and parameters are summarized in Table 1, and selected bond lengths and angles are given in Table 2.

Supplementary crystallographic data

CCDC 1451996 and 1451997 contain the supplementary crystallographic data for 1 and 2 in this article. These data can be obtained free of charge via http://www.ccdc. cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 UnionRoad, Cambridge CB21EZ, UK; Fax:(+44) 1223-336-033; or e-mail: deposit@ ccdc.cam.ac.uk.

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