

Electronic supplementary information for

Thermochromic properties of low-melting ionic uranyl isothiocyanate complexes

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CHN elemental analyses were performed on a CE Instruments EA-1110 elemental analyzer. ¹H NMR spectra were measured on a JEOL 400MHz NMR spectrometer unless otherwise specified. IR spectra were measured on a Shimadzu FTIR- 8400 spectrometer.

Synthesis of **[C₄mim]₃[UO₂(NCS)₅] (1)** : NH₄SCN (20 mmol, 1.522g), [C₄mim][SCN] (30 mmol, 5.92 g) and UO₂(ClO₄)₂•xH₂O (10 mmol) were dissolved in absolute ethanol and stirred for 12 hours at room temperature. The solvent was evaporated under reduced pressure and the residue was redissolved in dichloromethane. The precipitated NH₄ClO₄ was removed by filtration. The filtrate was cooled for 12 hours in a refrigerator at 4 °C and any further precipitate removed by filtration. The solvent was removed by a rotary evaporator and the product was dried under reduced pressure in a desiccator. Yield 83 %. CHN elemental analysis calcd.(%)for C₂₉H₄₅N₁₁O₂S₅U•H₂O (FW 996.11): C 34.96, H 4.76, N 15.47; found: C 34.45, H 4.29, N 15.07; IR (cm⁻¹): 2046 (-SCN); ¹H-NMR (400 MHz, CDCl₃): δ= 1.04 (t, 3H, *J* = 7.7 Hz, CH₂CH₂CH₂CH₃), 1.49 (m, 2H, CH₂CH₂CH₂CH₃), 2.06 (m, 2H, CH₂CH₂CH₂CH₃), 4.17 (s, 3H, CH₃), 4.44 (t, 2H, *J* = 7.8 Hz, CH₂CH₂CH₂CH₃), 7.77 (d, 2H, *J* = 7.8 Hz, CH), 9.07 (s, 1H, NCHN).

Synthesis of **[C₄mim]₄[(UO₂)(SCN)₆] (2)**: Complex **2** was prepared by changing the stoichiometric ratio of the initial reagents for the synthesis of complex **1**. Yield 87 %. calcd.(%) for C₃₈H₆₀N₁₄O₂S₆U: C, 38.83 H 5.15, N 16.68; found: C 38.96, H 5.41, N 16.61; IR (cm⁻¹): 2046 (SC≡N⁻); ¹H-NMR (CDCl₃): δ= 0.11 (t, 3H, *J* = 8.0 Hz, CH₂CH₂CH₂CH₃), 0.69 (m, 2H, CH₂CH₂CH₂CH₃), 1.41 (m, 2H, CH₂CH₂CH₂CH₃), 4.13 (s, 3H, CH₃), 4.43 (t, 2H, *J* = 7.8 Hz, CH₂CH₂CH₂CH₃), 8.61 (s, 1H, CH), 8.67 (s, 1H, CH), 10.26 (s, 1H, NCHN).

Synthesis of **[C₂mim]₃[(UO₂)(SCN)₅] (3)**: UO₂(NCS)₂·*n*H₂O ^[1] (0.440 g) was added to a round bottom flask containing [C₂mim][SCN] (0.507 g, 3.00 mmol) (IoLitec) and were dissolved in the 3:1 mixture of acetonitrile and methanol. After stirring for 48 hours, the solvent was evaporated, the powder formed was dried in a vacuum oven at 50 °C overnight. Yield 85 %. The product was analyzed by CHN elemental analysis calcd.(%) for C₂₃H₃₃N₁₁O₂S₅U: C, 30.90 H 3.72, N 17.24; found: C 30.34, H 2.59, N ; 16.48; IR (cm⁻¹): 2036 (SC≡N⁻); ¹H-NMR (Bruker 300 MHz, DMSO): δ= 1.41 (t, 3H, *J* = 7.3 Hz, CH₂CH₃), 3.83 (s, 3H, CH₃), 4.18 (m, 2H, -CH₂CH₃), 7.68 (s, 1H, CH), 7.77 (s, 1H, CH), 9.99 (s, 1H, NCHN).

Reference [1] R. D. Rogers, J. Zhang, D. T. Campbell, *J. Alloys Compd.* 1998, **271-273**, 133.

Time-Resolved Laser-Fluorescence Spectroscopy (TRLFS)

All samples were put into the non-luminescent cell mounted in a home-built liquid-nitrogen-cooled dewar of which the bottom was made of quartz. Dried air was blown over the outside of the quartz windows to avoid ice formation.

The excitation pulse used was the fourth harmonic generation of a Nd:YAG laser (Quantel) coupled with an optical parametric oscillator unit (Opotek INC.) to convert the wavelength of the laser light to 341 nm. The fluorescence of the sample was collected at right angle to the excitation beam and directed via two lenses into the entrance slit of the spectrograph (Shamrock RS 303i, 300 lines/mm, Andor Technology). The optically triggered signals from the PIN photo-diode to the controller in the PC software were adjusted through a delay generator (DG535, Stanford Research Inc.). The resulting spectra were measured by a time-gated ICCD camera (iStar, Andor Technology). The gate width was 25, 50, 100 μ s and the delay time after the excitation laser pulse of 10 μ s. Lifetime data were analyzed by Origin (Light Stone) software.

Details on the detection system can be found in reference [2].

Reference [2] T. Saito, H. Sao, K. Ishida, N. Aoyagi, T. Kimura, S. Nagasaki, S. Tanaka, *Environ. Sci. Technol.* 2010, **44**, 5055.

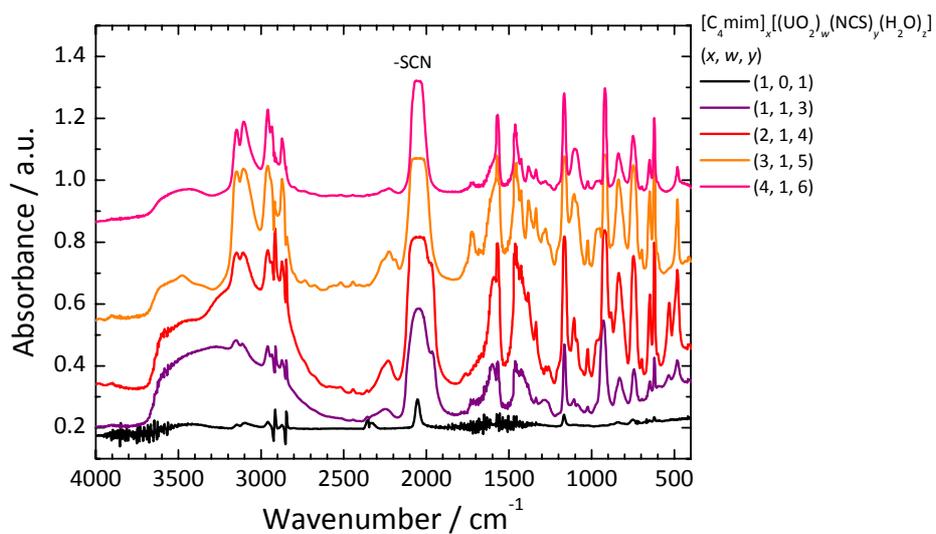


Figure S1. Infrared spectra of the ionic liquid [C₄mim][SCN] and the uranyl complexes [C₄mim]_x[(UO₂)_w(NCS)_y(H₂O)_z] at room temperature.

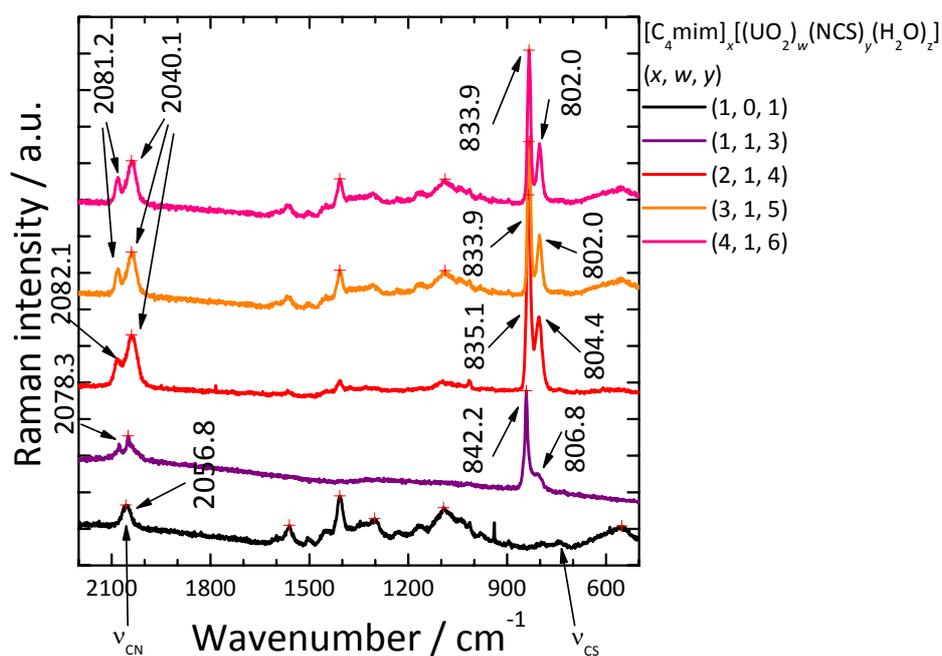


Figure S2. Raman spectra of the ionic liquid [C₄mim][SCN] and the uranyl complex [C₄mim]_x[(UO₂)_w(NCS)_y(H₂O)_z] at room temperature.

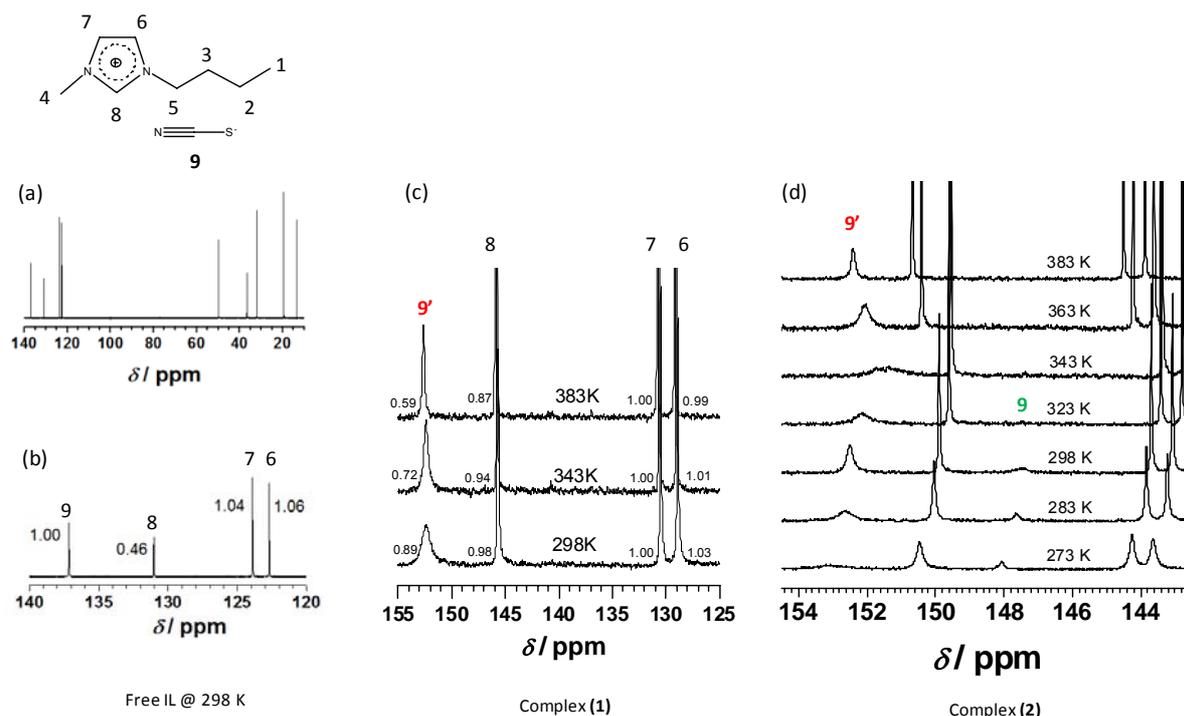


Figure S3. Temperature-dependent ^{13}C NMR spectra of the ionic liquid $[\text{C}_4\text{mim}][\text{SCN}]$, the uranyl complexes **1** and **2**. (a) Ionic liquid $[\text{C}_4\text{mim}][\text{SCN}]$, (b) Enlarged spectrum of lower magnetic field on (a), (c): complex **1**, (d) complex **2**.

In complex **1**, the resonance peak at 153 ppm (peak 9' in Fig. S3(c)) in the ^{13}C NMR spectra corresponding to SCN^- anions became narrower while keeping a constant chemical shift upon heating, while the spectral widths of the peaks due to the imidazolium cations did not change. When free thiocyanate ions are present (in complex **2**), a peak corresponding to the free ligand appeared in the spectrum at 148 ppm (peak 9 in Fig. S3(d)). This peak disappears above 343 K, because of the fast exchange with coordinated isothiocyanate ligands. Finally, a single narrow peak 9' was obtained at 383 K, indicating rapid exchange between coordinated ligands and free ligand ions at 383 K for complex **2**.

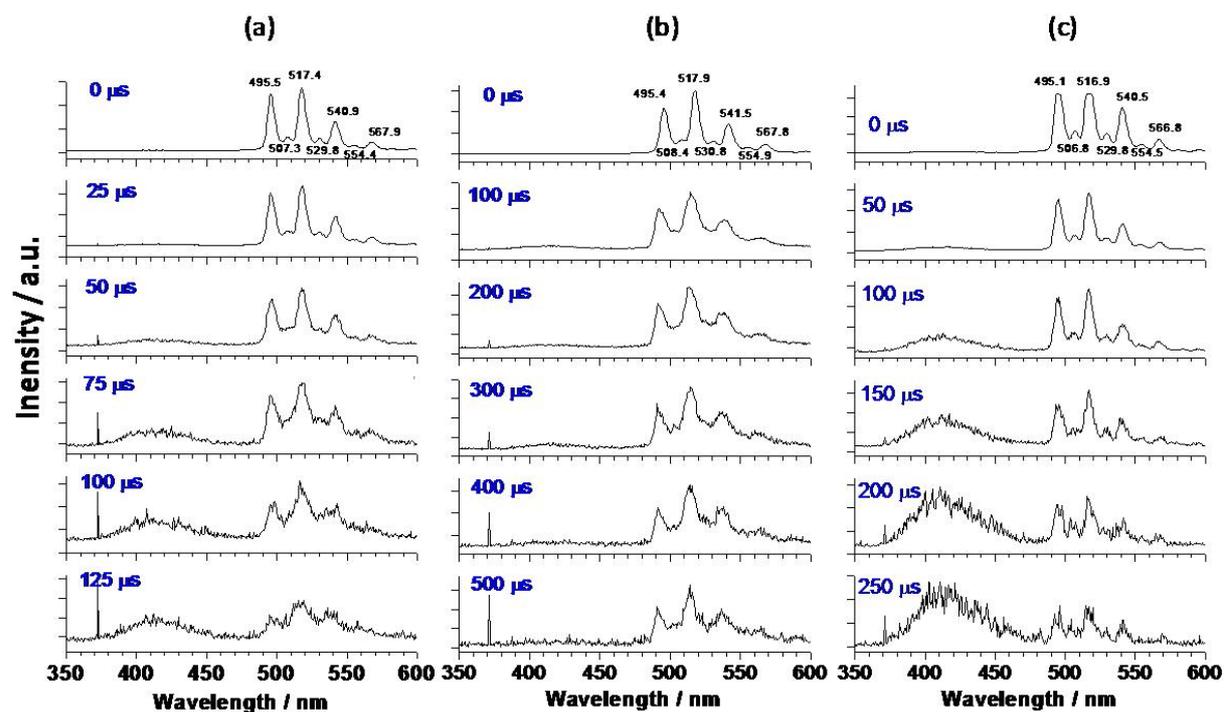


Figure S4. Time-resolved luminescence spectra of (a) 20 μ L of complex **1** in 500 μ L of acetonitrile, (b) complex **2** without solvent, (c): and 20 μ L of uranyl complex **2** in 500 μ L of acetonitrile. All the spectra were measured at 77 K. Excitation wavelength: $\lambda_{\text{ex}} = 341$ nm.

Table S1. Luminescence lifetimes obtained by biexponential curve fitting for the samples mentioned in Figure S5.

complex	solvent	$\tau_1 / \mu\text{s}$	$\tau_2 / \mu\text{s}$	λ_{em} / nm	assignment
(1)	MeCN	3.35	17.28	517.4	uranyl
		1.92	84.05	400-430	CT band
(2)	---	3.82	15	517.9	uranyl
		3.64	70.05	400-430	CT band
(2)	MeCN	13.68	73.63	516.9	uranyl
		4.06	93.94	400-430	CT band

Crystallographic data of [C₂mim]₃[UO₂(SCN)₅] (complex 3):

Yellow single crystals of complex **3** were obtained after 6 days by diffusion of diethyl ether into an ethanol solution of **3** at 16 °C. A crystal of **3** suitable for single crystal X-ray diffraction was mounted on a loop attached to a copper pin and placed in the cold N₂ stream at 100(2) K on a Bruker SMART 6000 diffractometer using Cu K α radiation ($\lambda = 1.54178\text{\AA}$). Absorption corrections were applied using the indexes of the crystal faces in XPREP^[1] and using SADABS.^[2] There was some ambiguity whether the space group was *C2/c* or *Cc*. In *C2/c* there are only 1.5 cations in the asymmetric unit and both the ‘whole cation’ and the ‘½ cation’ are disordered. Furthermore the ‘½ cation’ is situated on an inversion centre, symmetry that the C₂mim cation does not possess creating more disorder. In *Cc* there are three cations in the asymmetric unit, all on general positions, and only one is disordered. Therefore *Cc* was chosen because by refining it *C2/c* it would introduce disorder. E statistics are sometimes helpful in deciding between the centrosymmetric *C2/c* and the non-centrosymmetric *Cc* but these are by no means fool proof, especially when there are heavy atoms involved like here, so was not used an indicator in this case; for the record the $|E^*E-1|$ value is 0.71. The structure was solved using direct methods and refined by the full-matrix least-squares procedure in SHELXL.^[1] H atoms were placed in calculated positions and were refined using a riding model. A summary of the crystallographic data can be found below and the complete data in the CIF. The structure contained disorder of one C₂mim cation and three NCS anions. For the [C₂mim]⁺ cation occupancy of the major disorder component was 0.52(2). The geometry of the cation was restrained to be like the other two, not disordered, cations in the structure and the imidazolium ring along with its two carbon substituents were restrained to be flat. Restraints were also applied to the temperature factors. For all the NCS anions, the N–C, C–S and N—S distances were fixed to 1.15, 1.62 and 2.77 Å, respectively, to prevent the anions becoming too bent. In the three anions the occupancies of the major disorder components was found to be 0.517(12), 0.684(14) and 0.60(2). Restraints were also

applied to the temperature factors. The structure refined as an inversion twin and the scale factor refined to 0.518(19). The program OLEX2 was also used in refinement and making pictures.^[3] Crystallographic data for this paper and can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/conts/retrieving.html (or deposit@ccdc.cam.ac.uk).

[1] SHELXTL, version 5.1; Bruker AXS: Madison WI 1998.

[2] SADABS, version 5.0; an empirical absorption correction program from the SAINTPlus NT; Bruker AXS: Madison, WI 1998.

[3] OLEX2: a complete structure solution, refinement and analysis program; O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* 2009, **42**, 339.

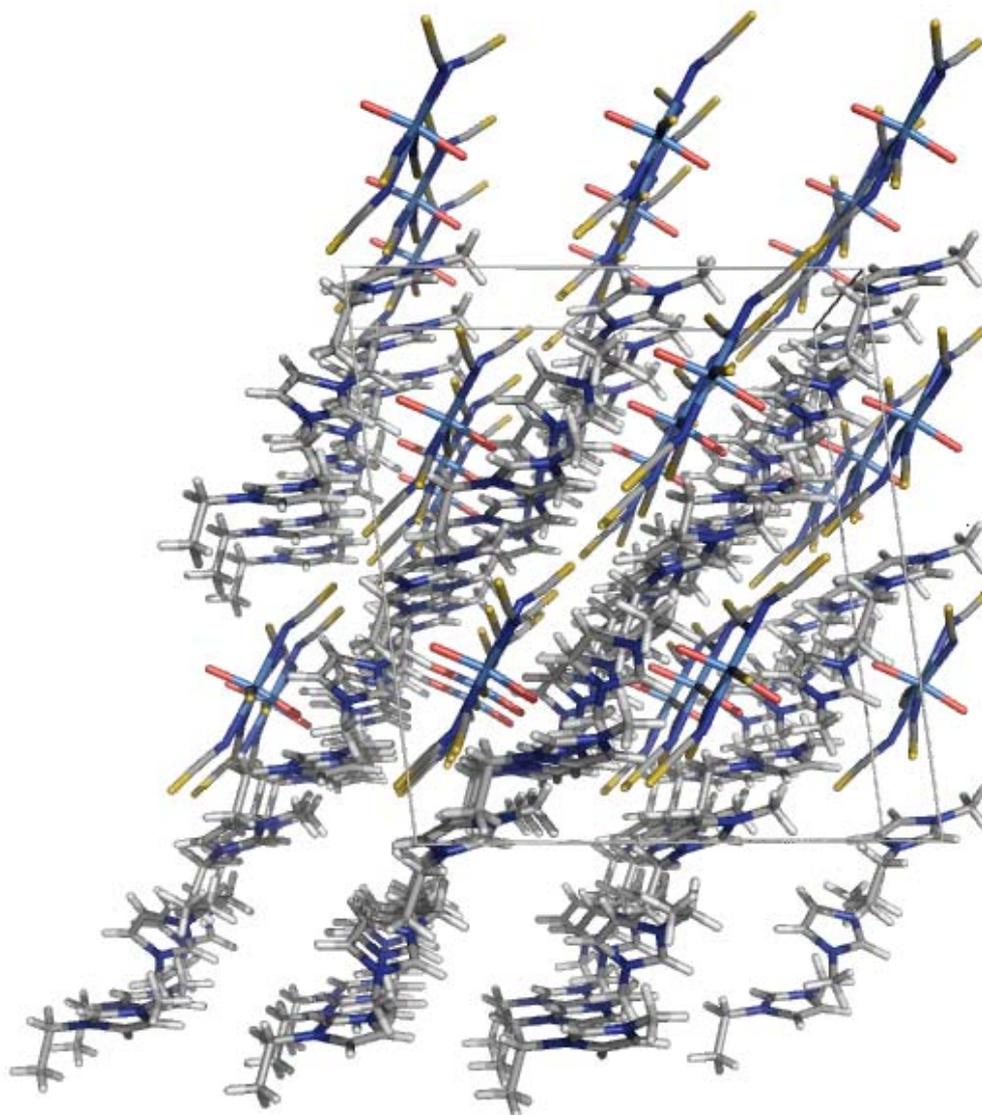


Figure S5. Packing in the crystal structure of complex 3.

Table S2. Crystallographic data of complex **3** and selected bond distances (Å) and bond angles (°) of complex **3** with standard uncertainties in parentheses.

[C ₂ mim] ₃ [UO ₂ (SCN) ₅]	
formula	C ₂₃ H ₃₃ N ₁₁ S ₂ O ₅ U
<i>M</i>	893.93
crystal system	monoclinic
space group	<i>Cc</i>
<i>a</i> [Å]	17.6459(12)
<i>b</i> [Å]	12.6743(9)
<i>c</i> [Å]	15.7555(13)
α [°]	90
β [°]	97.081(4)
γ [°]	90
<i>V</i> [Å ³]	3496.8(4)
$\rho_{\text{calcd.}}$ [g cm ⁻³]	1.698
μ [mm ⁻¹]	16.18
<i>T</i> [K]	100(2)
measured refl.	13956
indep.refl.	5800
<i>R</i> _{int} (%)	6.51
obs.refl.	5000
<i>F</i> (000)	1744
<i>R</i> ₁ (obs) (%)	6.37
w <i>R</i> ₂ (all) (%)	17.56
GooF	1.021
# of parameters	435

Bond distances	/ Å
U-O(1)	1.766(8)
U-O(2)	1.765(9)
U-N(1)	2.513(10)
U-N(2)	2.494(12)
U-N(3)	2.398(11)
U-N(4)	2.429(9)
U-N(5)	2.434(6)
U-N(1')	2.520(9)
U-N(2')	2.503(9)
U-N(5')	2.429(8)

Bond angles	/ °
O2 U1 O1	171.2(9)
O2 U1 N3	87.4(8)
O1 U1 N3	84.6(7)
O2 U1 N4	89.2(9)
O1 U1 N4	85.6(8)
N3 U1 N4	77.5(6)
O2 U1 N5'	87.6(13)
O1 U1 N5'	93.2(13)
N3 U1 N5'	71.5(14)
N4 U1 N5'	149.0(13)
O2 U1 N5	89.5(11)
O1 U1 N5	89.9(11)
N3 U1 N5	62.7(10)
N4 U1 N5	140.3(10)
N5' U1 N5	9.1(8)
O2 U1 N2	95.4(11)
O1 U1 N2	90.4(10)
N3 U1 N2	154.8(9)
N4 U1 N2	77.4(8)
N5' U1 N2	133.5(14)
N5 U1 N2	142.2(11)
O2 U1 N2'	91.7(10)
O1 U1 N2'	93.3(9)
N3 U1 N2'	148.5(7)
N4 U1 N2'	71.0(4)
N5' U1 N2'	139.9(14)
N5 U1 N2'	148.7(10)
N2 U1 N2'	7.3(8)
O2 U1 N1	93.8(10)
O1 U1 N1	94.8(9)
N3 U1 N1	142.2(8)
N4 U1 N1	140.2(8)
N5' U1 N1	70.7(14)
N5 U1 N1	79.5(11)
N2 U1 N1	62.8(9)
N2' U1 N1	69.3(8)
O2 U1 N1'	97.6(11)
O1 U1 N1'	90.8(10)
N3 U1 N1'	137.1(7)
N4 U1 N1'	144.7(10)
N5' U1 N1'	66.2(16)
N5 U1 N1'	74.7(13)
N2 U1 N1'	67.5(11)
N2' U1 N1'	74.2(10)
N1 U1 N1'	6.2(9)