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Introduction

Uranium is the most important element in nuclear engineering. The chemistry of uranium plays important roles in nuclear fuel fabrication and spent fuel reprocessing. Under ambient conditions, uranium is most commonly present as a hexavalent uranyl(vi) ion, $UO_2^{2^+}$, with a typical linear $[O \equiv U^{VI} \equiv O]^{2^+}$ structure. The chemical separation of $UO_2^{2^+}$ from various aqueous systems such as feed solutions of spent nuclear fuels and even seawater is one of the important research topics in nuclear chemistry. In the usual sense, coordination chemistry provides very powerful tools for chemical separation. Hence, the

Effects of coordinating heteroatoms on molecular structure, thermodynamic stability and redox behavior of uranyl(vi) complexes with pentadentate Schiff-base ligands[†]

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Uranyl(v) complexes with pentadentate N_3O_2 -, N_2O_3 - and $N_2O_2S_1$ -donating Schiff base ligands, tBu,MeOsaldien $-X^{2-}$ (X = NH, O and S), were synthesized and thoroughly characterized by ¹H NMR, IR, elemental analysis, and single crystal X-ray diffraction. The crystal structures of UO₂(tBu,MeO-saldien-X) showed that the U-X bond strength follows U-O \approx U-NH > U-S. Conditional stability constants (β_X) of UO₂(tBu,MeO-saldien-X) in ethanol were investigated to understand the effect of X on thermodynamic stability. The log β_X decrease in the order of UO₂(tBu,MeO-saldien-NH) (log $\beta_{NH} = 10) > UO_2(tBu,MeO$ saldien–O) (log $\beta_{\rm O}$ = 7.24) > UO₂(tBu,MeO-saldien–S) (log $\beta_{\rm S}$ = 5.2). This trend cannot be explained only by Pearson's Hard and Soft Acids and Bases (HSAB) principle, but rather follows the order of basicity of X. Theoretical calculations of UO₂(tBu,MeO-saldien-X) suggested that the ionic character of U-X bonds decreases in the order of U–NH > U–O > U–S, while the covalency increases in the order U–O < U–NH < U-S. Redox potentials of all UO₂(tBu.MeO-saldien-X) in DMSO were similar to each other regardless of the difference in X. Spectroelectrochemical measurements and DFT calculations revealed that the center U⁶⁺ of each UO₂(tBu,MeO-saldien-X) undergoes one-electron reduction to afford the corresponding uranyl(v) complex. Consequently, the difference in X of UO₂(tBu,MeO-saldien-X) affects the coordination of tBu,MeO-saldien- X^{2-} with UO_2^{2+} . However, the HSAB principle is not always prominent, but the Lewis basicity and balance between ionic and covalent characters of the U-X interactions are more relevant to determine the bond strengths.

complexation between ${\rm UO_2}^{2^+}$ and organic ligands has been widely studied. $^{1\text{-}13}$

Pearson's Hard and Soft Acids and Bases (HSAB) principle is quite useful to describe preferential interactions between specific metal ions and coordinating atoms of ligands and to design organic molecules selectively coordinating with a target metal ion,14,15 although this principle is rather empirical. In the HSAB principle, UO2²⁺ is classified as a hard acid,^{14,15} and therefore, generally tends to more strongly interact with hard bases like N, O and F, compared with softer ones such as heavier congeners like P, S, and Cl.14,15 Indeed, thermodynamic stability of a UO₂²⁺-halido complex in DMF follows the order of hardness of halide ligands, $Cl^- > Br^- > I^{-16}$. In contrast, such a trend in complexation between UO_2^{2+} and heteroatoms like N, O and S, seems not to be well understood systematically, although it would provide essential information to understand the fundamental nature of UO2²⁺ in more depth and to design molecular structures of ligands exclusively interacting with UO2²⁺. Indeed, several extracting reagents have been successfully developed for separation of Am(III) and Cm(III) from Ln(III) on the basis of difference in coordinating affinities of these metal ions with soft-donor atoms incorporated in the designed ligands.17-20

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[†] Electronic supplementary information (ESI) available: Crystallographic data of $UO_2(L_X)$, crystal structure of H_2L_S , electrochemical data, spectroelectrochemical data, and optimized structures and structural parameters of $[UO_2(L_X)]^{-/0}$. CCDC 2177295 for $UO_2(L_O) \cdot (C_5H_5N)$, 2177296 for $UO_2(L_S) \cdot (CH_2Cl_2)$ and 2177297 for $UO_2(L_{NH}) \cdot (CH_2Cl_2)$. For ESI and crystallographic data in CIF or other electronic format see https://doi.org/10.1039/d2ra04639c



Fig. 1 Schematic structures of $UO_2(R_1, R_2, -R_saldien)^{21,22}$ (a) and $UO_2(tBu, MeO-saldien-X)$ complexes ($UO_2(L_X)$); (X = NH, O, S) (b).

In this study, we discuss strengths of U–N, U–O and U–S interactions formed in $UO_2^{2^+}$ complexes having analogous coordination geometries. For this purpose, it is first necessary to choose a suitable ligand system. Previously, we reported $UO_2^{2^+}$ complexes with N₃O₂-pentadentate Schiff base ligands, $UO_2(R_1,R_2,-^R saldien)$, shown in Fig. 1(a).^{21,22} Its NR moiety can be substituted with O or S to provide the similar $UO_2^{2^+}$ complexes, $UO_2(tBu,MeO-saldien-X)$ ($UO_2(L_X)$, X = NH, O, S, Fig. 1(b)), where the U–O or U–S bond will be formed instead of U–NR. Here, we report synthesis and characterization of $UO_2(L_X)$ (X = NH, O, S) to discuss effects of X to the U–X bond strength and thermodynamic stability as well as redox chemistry of this class of $UO_2^{2^+}$ complexes.

Experimental section

Materials and syntheses

All reagents used were of reagent grade and used as received, if not specified. 3-*tert*-Butyl-5-methoxysalicylaldehyde was synthesized as reported elsewhere.²³

UO₂(tBu,MeO-Saldien-NH) (UO₂(L_{NH})). To a solution of 3tert-butyl-5-methoxysalicylaldehyde (202 mg, 0.971 mmol) in ethanol (2 mL) was added 2,2'-diaminodiethylamine (52.1 µL, 0.480 mmol). This solution was heated to reflux for 10 min. UO₂(NO₃)₃·6H₂O (210 mg, 0.418 mmol) dissolved in ethanol (2 mL) was dropwise added to the solution. A red precipitate was formed within several minutes, and the suspension was stirred at 60 °C for 1 h. After cooling to room temperature, a red precipitate was collected by filtration and rinsed with methanol. Recrystallization from CH2Cl2/ethanol yielded red crystals. Yield: 176 mg (48%). This compound was characterized by ¹H NMR, IR and elemental analysis. ¹H NMR (399.78 MHz, CD₂Cl₂, δ/ppm vs. TMS): 1.71 (s, 18H, -C(CH₃)₃), 3.61 (m, 2H, C=N- CH_2CH_2 -N or C=N-CH₂CH₂-N), 3.83 (s, 6H, O-CH₃), 4.07 (m, 2H, C=N-CH₂CH₂-N or C=N-CH₂CH₂-N), 4.26 (m, 1H, -NH), 4.50 (m, 4H, C=N-CH₂CH₂-N or C=N-CH₂CH₂-N), 6.86 (d, 2H, aryl, $J_{H-H} = 3.2$ Hz), 7.32 (d, 2H, aryl, $J_{H-H} = 3.2$ Hz), 9.38 (s, 2H, N=CH-). ¹H NMR (399.78 MHz, DMSO-*d*₆, δ/ppm *vs.* TMS): 1.65 (s, 18H, $-C(CH_3)_3$), 3.40 (m, 2H, C=N-CH₂CH₂-N or C=N-CH₂CH₂-N), 3.75 (s, 6H, O-CH₃), 4.02 (m, 2H, C=N-CH₂CH₂-N or C=N-CH₂CH₂-N), 4.49 (m, 4H, C=N-CH₂CH₂-N or C=N-CH₂CH₂-N), 6.51 (m, 1H, -NH), 7.04 (d, 2H, aryl, *J*_{H-H} = 3.2 Hz), 7.14 (d, 2H, aryl, $J_{H-H} = 3.2$ Hz), 9.57 (s, 2H, N=CH-). IR

(ATR, cm⁻¹): 858 (O=U=O asymmetric stretching, ν_3), 1636 (C=N stretching, $\nu_{C=N}$). Elemental analysis (%) calcd for **UO₂(L_{NH})** (C₂₈H₃₉N₃O₆U₁): C, 44.74; H, 5.23; N, 5.59. Found: C 44.64; H, 5.29; N, 5.42. The obtained crystals were also suitable for the X-ray crystallography.

 $UO_2(tBu, MeO-Saldien-O)$ ($UO_2(L_O)$). To a solution of 3-tertbutyl-5-methoxysalicylaldehyde (50.7 mg, 0.243 mmol) in ethanol (3 mL) was added 2,2'-oxybis(ethylamine) (12.6 µL, 0.119 mmol). This solution was heated to reflux for 10 min. $UO_2(NO_3)_3 \cdot 6H_2O$ (210 mg, 0.418 mmol) dissolved in ethanol (2 mL) was dropwise added to the solution. A red precipitate was formed within several minutes, and the suspension was stirred at 60 °C for 1 h. After cooling to room temperature, a red precipitate was collected by filtration and rinsed with methanol. Recrystallization from CH₂Cl₂/ethanol yielded red microcrystals. Yield: 27.1 mg (30%). This compound was characterized by ¹H NMR, IR and elemental analysis. ¹H NMR (399.78 MHz, CD_2Cl_2 , δ /ppm vs. TMS): 1.71 (s, 18H, $-C(CH_3)_3$), 3.83 (s, 6H, O-CH₃), 4.59 (m, 4H, C=N-CH₂CH₂-O or C=N-CH₂CH₂-O), 4.65 (m, 4H, C=N-CH₂CH₂-O or C=N-CH₂CH₂-O), 6.91 (d, 2H, aryl, *J*_{H-H} = 3.2 Hz), 7.33 (d, 2H, aryl, *J*_{H-H} = 3.6 Hz), 9.50 (s, 2H, N=CH-). ¹H NMR (399.78 MHz, DMSO-*d*₆, δ/ppm νs. TMS): 1.64 (s, 18H, -C(CH₃)₃), 3.77 (s, 6H, O-CH₃), 4.53 (t, 4H, C=N- CH_2CH_2 -O or C=N-CH₂CH₂-O, $J_{H-H} = 5.2$ Hz), 4.66 (t, 4H, C= N-CH₂CH₂-O or C=N-CH₂CH₂-O, $J_{H-H} = 5.2$ Hz), 7.09 (d, 2H, aryl, $J_{H-H} = 3.2$ Hz), 7.17 (d, 2H, aryl, $J_{H-H} = 3.6$ Hz), 9.75 (s, 2H, N=CH-). IR (ATR, cm^{-1}): 883 (O=U=O asymmetric stretching, ν_3), 1637 (C=N stretching, $\nu_{C=N}$). Elemental analysis (%) calcd for UO₂(L₀) (C₂₈H₃₈N₂O₇U₁): C, 44.68; H, 5.09; N, 3.72. Found: C 44.79; H, 5.21; N, 3.65. The crystals suitable for X-ray diffraction were obtained by recrystallization from pyridine/hexane.

UO₂(*t*Bu,MeO–Saldien–S) (UO₂(L_s)). To a solution of 3-*tert*butyl-5-methoxysalicylaldehyde (54.4 mg, 0.261 mmol) in ethanol (3 mL) was added 2,2'-thiobis(ethylamine) (14.5 μ L, 0.126 mmol). This solution was heated to reflux for 10 min under Ar. UO₂(NO₃)₃·6H₂O (210 mg, 0.418 mmol) dissolved in ethanol (2 mL) was dropwise added to the solution under Ar. A dark red precipitate was formed within several minutes, and the suspension was stirred at 60 °C for 1 h. After cooling to room temperature, a red precipitate was collected by filtration quickly, and rinsed with deoxygenated ethanol. Recrystallization from CH₂Cl₂/ethanol yielded dark red plate crystals. Yield: 7.8 mg (8%). This compound was characterized by ¹H NMR, IR and elemental analysis. ¹H NMR (399.78 MHz, CD₂Cl₂, δ /ppm vs. TMS): 1.70 (s, 18H, -C(CH₃)₃), 3.74 (br, 4H, C=N-CH₂CH₂-S or C=N-CH₂CH₂-S), 3.83 (s, 6H, O-CH₃), 3.74 (s, 4H, C=N-CH₂CH₂-S or C=N-CH₂CH₂-S), 5.33 (s, 1H, CH₂Cl₂), 6.89 (d, 2H, Aryl, *J*_{H-H} = 3.2 Hz), 7.33 (d, 2H, aryl, *J*_{H-H} = 3.6 Hz), 9.47 (s, 2H, N=CH-). ¹H NMR (399.78 MHz, DMSO-*d*₆, δ /ppm vs. TMS): 1.64 (s, 18H, -C(CH₃)₃), 3.77 (s, 6H, O-CH₃), 3.79 (br, 4H, C=N-CH₂CH₂-S or C=N-CH₂CH₂-S), 4.60 (br, 4H, C=N-CH₂CH₂-S or C=N-CH₂CH₂-S), 7.09 (d, 2H, aryl, *J*_{H-H} = 3.2 Hz), 7.18 (d, 2H, aryl, *J*_{H-H} = 2.8 Hz), 9.74 (s, 2H, N=CH-). IR (ATR, cm⁻¹): 880 (O=U=O asymmetric stretching, *v*₃), 1623 (C=N stretching, *v*_{C=N}). Elemental analysis (%) calcd for **UO**₂(**L**_S)·0.5CH₂Cl₂ (C₂₈H₃₈N₂O₆S₁U₁·0.5CH₂Cl₂): C, 42.20; H, 4.85; N, 3.45. Found: C 42.24; H, 4.79; N, 3.40. The obtained crystals were also suitable for the X-ray crystallography.

Methods

The ¹H NMR spectra were recorded by using JEOL ECX-400 (¹H: 399.78 MHz) NMR spectrometer. The chemical shifts of ¹H NMR were referenced to TMS ($\delta = 0$ ppm). The IR measurements were performed by JASCO FT/IR4700 equipped with a diamond ATR attachment. Elemental analyses were carried out by Yanaco MT-6 CHN elemental analyzer. Cyclic voltammetry (CV) measurements of $UO_2(L_x)$ (1 mM) dissolved in DMSO containing 0.1 M tetra-n-butylammonium perchlorate (TBAP) were performed at 295 K under a dry Ar atmosphere by using BAS ALS660B electrochemical analyzer. A three-electrode system consisted of a Pt disk working electrode (diameter: 1.6 mm, surface area: 0.020 cm²), a Pt wire counter electrode, and an $Ag^{0/+}$ reference electrode (0.1 M TBAP + 1 mM $AgNO_3/$ CH₃CN). A ferrocene/ferrocenium ion redox couple ($Fc^{0/+}$) was taken as an external standard redox system. All samples were prepared under an inert Ar atmosphere. Dissolved oxygen gas in each sample solution was expelled by purging Ar gas for at least 10 min prior to starting the CV experiments. UV-vis-NIR spectroelectrochemical measurements in DMSO were performed with a JASCO V-770 spectrophotometer equipped with an optically transparent thin layer electrode (OTTLE) cell at 295 K.²⁴⁻²⁷ Its optical path length was 1.0×10^{-2} cm, which was calibrated spectrophotometrically.22 The three-electrode system was the same as that in the above electrochemical experiments with a replacement of the working electrode by a Pt gauze (80 mesh). The potential applied on OTTLE was controlled by BAS ALS660B. The absorption spectrum at each potential step was recorded after equilibration of the electrochemical reaction at the applied potential on the working electrode, which completed within 3 min. The sample solution in the OTTLE cell was prepared in a similar manner to that for the CV measurements.

Crystallographic analysis

The X-ray diffraction data of the well-shaped single crystals of $UO_2(L_{NH}) \cdot (CH_2Cl_2)$, $UO_2(L_0) \cdot (C_5H_5N)$ and $UO_2(L_s) \cdot (CH_2Cl_2)$ were collected by a Rigaku XtaLAB mini II equipped with hybrid pixel array detector and graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Each sample was mounted on a MiTeGen

Dual Thickness MicroMounts, and located in the temperaturecontrolled N₂ gas flow. Intensity data were collected by taking oscillation photographs. Reflection data were corrected for both Lorentz and polarization effects. The structures were solved by the direct method and refined anisotropically by the SHELX program suite²⁸ for non-hydrogen atoms by full-matrix leastsquares calculations. Each refinement was continued until all shifts were smaller than one-third of the standard deviations of the parameters involved. Hydrogen atoms were located at the calculated positions. All hydrogen atoms were constrained to ideal geometry with C-H = 0.95 Å. The thermal parameters of all hydrogen atoms were related to those of their parent atoms by $U(H) = 1.2U_{eq}(C)$. All calculations were performed by using the Olex2 crystallographic software program package.29 Crystallographic data of all complexes were summarized in Table S1,† and deposited with Cambridge Crystallographic Data Centre as supplementary publication no: CCDC 2177295 $(UO_2(L_0) \cdot (C_5H_5N))$, 2177296 $(UO_2(L_{NH}) \cdot (CH_2Cl_2))$, and 2177297 $(UO_2(L_s) \cdot (CH_2Cl_2)).$

UV-vis titration

Sample solutions of H_2L_X (X = NH, O, S, 0.1 mM) were prepared by mixing 3-tert-butyl-5-methoxysalicylaldehyde and the corresponding diamines in ethanol. The formation of H_2L_X (X = NH, O, S) was checked by ¹H NMR spectroscopy (see Fig. S1[†]). Triethylamine (NEt₃, 0.4 mM) was added as a H⁺ scavenger after the formation of $UO_2(L_x)$. The total concentration of UO_2^{2+} was stepwise increased up to 0.12 mM ($0 \le [UO_2^{2^+}]/[L_X^{2^-}] \le 1.2$) by adding a feed solution of $UO_2(NO_3)_3 \cdot 6H_2O(10 \text{ mM})$ in ethanol. The UV-vis absorption spectrum at each increment step was recorded by JASCO V-770 spectrophotometer. During the whole titration experiment, temperature of the sample solution was kept at 293 K in a thermostat cell holder equipped with the spectrophotometer. The obtained titration series of the UV-vis absorption spectra was analyzed by HypSpec (version 1.1.33)³⁰ to determine conditional stability constants of $UO_2(L_x)$ (X = NH, O, S) under the presence of 0.4 mM NEt₃ in ethanol.

Theoretical calculations

Density functional theory (DFT) calculations were performed using Gaussian 16 program (Revision B.01)³¹ for characterization of $UO_2(L_x)$ and the one-electron reduced complexes, $[UO_2(L_X)]^-$ (X = NH, O, S). The atomic coordinates of $UO_2(L_X)$ were taken from those experimentally-determined and were used for structure optimization. Hybrid DFT functional B3LYP32 was employed and solvent was modelled through a conductorlike polarized continuum model (CPCM) for DMSO (dielectric $\varepsilon = 46.7$).³³ For uranium, Stuttgart-type small-core effective core potential (ECP) and corresponding basis set has been used.34 The most diffuse basis functions on uranium with the exponent 0.005 (all s, p, d, and f type functions) were omitted as in previous studies.³⁵⁻³⁹ The 6-311G(d) basis sets were used for other elements (C, H, N, O, S). Vibrational frequency calculations at the same level of theory confirmed that no imaginary frequency was found to be present. Single-point calculations for energetic analysis were performed using the same condition.

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NBO analysis were carried out by using the NBO 5.0 program.⁴⁰ The molecular structures of $[UO_2(L_x)]^-$ were taken from those of $UO_2(L_x)$ determined experimentally and were optimized after addition of a single negative charge and doublet spin degeneracy to assume the one-electron reduction using the same condition. The Mulliken spin-density plots were illustrated by GaussView 6.1.⁴¹

Results and discussion

Synthesis and structure determination of $UO_2(L_X)$ (X = NH, O, S)

Each ligand was synthesized through a condensation reaction between a 3-*tert*-butyl-5-methoxysalicylaldehyde and the corresponding diamine in ethanol, and further reacted with one equivalent of $UO_2(NO_3)_2 \cdot 6H_2O$ to afford $UO_2(L_x)$. These complexes were yielded as red microcrystalline solids, which were recrystallized from appropriate solvent mixtures to obtain single crystals suitable for X-ray structure determination. The IR peaks of $[O \equiv U \equiv O]^{2+}$ asymmetric stretching (ν_3) and $C \equiv N$ stretching ($\nu_{C=N}$) of $UO_2(L_x)$ were observed at around 860–880 and 1630 cm⁻¹, respectively. The elemental analysis for $UO_2(L_x)$ well-agreed with the expected chemical formulae of them.

The molecular structures of $UO_2(L_x)$ were determined by single crystal X-ray diffraction (SCXRD). The resulting molecular structures of $UO_2(L_x)$ are shown in Fig. 2 and S2.[†] The selected bond lengths of them are summarized in Table 1. As a general trend, $UO_2^{2^+}$ in $UO_2(L_x)$ is five-coordinated in its equatorial plane to give a pentagonal bipyramidal coordination geometry as expected in Fig. 1(b), which is typically found in $UO_2^{2^+}$ complexes.^{21,22}

The U= O_{ax} bond lengths of UO₂²⁺ in UO₂(L_x) (U(1)–O(1), U(1)–O(2)) are 1.78–1.79 Å, which is similar to those in UO₂²⁺ complexes reported previously.^{21,22} Herein, we introduced *tert*-butyl groups at the *ortho*-positions of the phenolate moieties in each system to control the structure of the ligand after coordination to UO₂²⁺. To avoid steric collision between these bulky groups in UO₂(L_x), two phenolate moieties are forced to be present in the opposite sides of the equatorial plane of UO₂²⁺ (Fig. 2 and S2†). Such a twisted structure of a planar pentadentate ligand was also observed in the saldien-type ligands (*e.g.*, Fig. 1(a)) we reported previously.^{21,22}

The bond angles around X are strongly affected by the difference in X. The mean bond angle of C(9)-N(3)-C(10), C(9)-

Table 1 Selected bond lengths (Å) of $UO_2(L_X)$ (X = NH, O, S)

	UO ₂ (LNH)	UO ₂ (LO)	UO ₂ (LS)
U. O(1)	1 702(0)	1 702(2)	1 77((5)
0 - 0(1)	1.793(2)	1.792(2)	1.776(5)
U-O(2)	1.787(2)	1.790(2)	1.778(5)
U-O(3)	2.238(2)	2.239(2)	2.241(6)
U-O(4)	2.239(2)	2.239(2)	2.231(5)
U-N(1)	2.535(3)	2.523(3)	2.543(7)
U-N(2)	2.554(2)	2.531(3)	2.542(6)
U–X	2.594(5)	2.581(3)	2.981(2)
C(1)-O(3)	1.342(3)	1.332(3)	1.34(1)
C(18)-O(4)	1.333(3)	1.334(3)	1.34(1)

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N(3)-U(1) and C(10)-N(3)-U(1) in $UO_2(L_{NH})$ is 111°, which is close to the ideal value (109.5°) of the tetrahedral coordination around N, showing its sp³ character. Note that the N-H moiety in $UO_2(L_{NH})$ forms a hydrogen bond with the axial O of UO_2^{2+} of the neighboring complexes (D···A: 3.15 Å, D–H: 1.00 Å, H···A: 2.210 Å, D–H…A: 154.9°). Nevertheless, there seems to be little effect on the structure of this UO2²⁺ complex, because the similar bond angles around N was also observed in UO2(*t*Bu,MeO-^{Me}saldien) (109°, see Fig. 1). The mean bond angles around X in $UO_2(L_0)$ and $UO_2(L_s)$ are 120° and 98°. Moreover, the deviation of X from the mean planes defined by U1, N1, N2, O3, and O4 in $UO_2(L_S)$ (0.489 Å) is larger than those of $UO_2(L_{NH})$ (0.261 Å) and UO₂(L₀) (0.116 Å). Such a difference would be related to the bonding nature and steric factor of these X atoms. However, it is difficult at this moment to clearly describe in detail how the hardness/softness of X affects such a structural trend. Hence, we decided to focus on the bond lengths around X as another structural parameter directly affected by the coordination strength.

In the UO₂(L_x) complexes studied here, the bond lengths between U and the phenolic O (U(1)–O(3), U(1)–O(4)) are 2.23– 2.24 Å regardless of difference in X. This is also the case for those between U and the imino N (U(1)–N(1), U(1)–N(2), 2.52– 2.55 Å). In contrast, the U(1)–X bond lengths depend on X. The U(1)–N(3) distance of UO₂(L_{NH}) is 2.594(5) Å, which is slightly longer than the corresponding interaction in UO₂(L_O) (U(1)– O(5) = 2.581(3) Å). These bond lengths are commonly found in the previous reports.^{21,22} The U(1)–S(1) distance in UO₂(L_S) is significantly longer than the others. However, the U(1)–S(1) distance of UO₂(L_S) is still shorter than the sum of van der Waals radii of U and S (2.3 Å + 1.8 Å = 4.1 Å),⁴² suggesting that chemical bonding interaction is certainly present between U(1)



Fig. 2 ORTEP views of UO₂(L_{NH}) (a), UO₂(L_O) (b), UO₂(L_S) (c). Ellipsoids are at 50% probability level. Hydrogen atoms and solvent molecules were omitted for clarify.

and S(1) in this complex. Indeed, the U(1)–S(1) distance of $UO_2(L_S)$ (2.981(2) Å) is close to the U–S bond lengths in $UO_2^{2^+}$ -thioether complexes reported previously (2.96–3.02 Å).^{2,43,44} The observed structural parameters of the U–X interactions in $UO_2(L_x)$ are quite common in uranyl complexes having X atom coordination reported so far.^{2,21,22,43,44} Therefore, $UO_2(L_X)$ studied here are suitable for exploring impacts of X in the coordination chemistry of $UO_2^{2^+}$.

It could be misleading to discuss the strengths of the U–X bonding interactions solely on the basis of the observed bond lengths, because the sizes of N, O and S are different from each other. The bond strengths between two atoms can be normalized by reduction in an interaction distance (R_{UX}) derived from the sum of van der Waals radii and an actual bond length between U and X as shown in eqn (1).^{45–47}

$$R_{\rm UX} = (d_{\rm UX})/(r_{\rm U} + r_{\rm X})$$
(1)

where $r_{\rm U}$ and $r_{\rm X}$, are van der Waals radii of U and X, respectively. $d_{\rm UX}$ is the U-X bond length of $\rm UO_2(L_X)$ determined by SCXRD.⁴⁵⁻⁴⁷ Based on this definition, greater R_{UX} implies weaker U-X bond (vice versa). As a result, $R_{\rm UX}$ of $\rm UO_2(L_{\rm NH})$ is 0.665, which is close to that of $UO_2(L_0)$ (0.670). This implies that the bond strengths of U(1)-N(3) in $UO_2(L_{NH})$ and U(1)-O(5) in $UO_2(L_0)$ are similar to each other. In contrast, R_{UX} of $UO_2(L_s)$ is 0.727, which is significantly greater than those of $UO_2(L_{NH})$ and $UO_2(L_0)$. Hence, the U(1)-S(1) bond strength of $UO_2(L_S)$ is supposed to be weaker than the U-X ones in $UO_2(L_{NH})$ and $UO_2(L_0)$. Consequently, the bond strength of U-X interactions follows U–O \approx U–NH > U–S. As widely accepted in the HSAB principle, the hardness of X moiety follows O > NH > S.^{14,15} Therefore, the trend of U–X bond strengths of $UO_2(L_x)$ cannot be explained only by the HSAB principle, while the bond strength of U(1)-S(1) of $UO_2(L_S)$ is certainly weaker than others. Note that all R_{UX} of $UO_2(L_X)$ presented here are much smaller than those of noncovalent intermolecular interactions such as Cl···X and hydrogen bonds reported previously, where R = 0.98-0.80.45-47 Therefore, a coordination bond is certainly formed between U and X in each $UO_2(L_x)$.

Thermodynamic stability of $UO_2(L_X)$ (X = NH, O, S)

In the crystal structures of $UO_2(L_x)$ (X = NH, O, S), the U–X bond strength depends on the difference in X. Therefore, there would also be some impact on the thermodynamic stability of $UO_2(L_x)$. To confirm this issue, we investigated the complexation of $UO_2^{2^+}$ and $L_x^{2^-}$ in ethanol by spectrophotometric titration. Fig. 3 shows the UV-vis absorption spectra recorded at different total concentration ratios between $UO_2^{2^+}$ and $L_x^{2^-}$ represented by C_U/C_L . Note that these titration experiments were conducted under the presence of 0.4 mM NEt₃ employed as a H⁺ scavenger after the formation of $UO_2(L_x)$.

In all titration series shown in Fig. 3, the absorbance at 370 nm and 425 nm increased with an increase in C_U/C_L . Simultaneously, the absorption intensity at 350 nm decreased. The isosbestic points were clearly observed, indicating that the complexation equilibrium between UO_2^{2+} and L_X^{2-} only takes place in each system. As shown in the insets of Fig. 3(a) and (b), the absorbance at 370 nm tends to be saturated at $C_U/C_L = 1.0$, indicating that $UO_2(L_{NH})$ and $UO_2(L_O)$ are almost quantitatively formed. On the other hand, such a trend is equivocal for X = S (Fig. 3(c)), implying that the weaker coordination of L_S^{2-} .

To estimate the conditional stability constants ($\beta_x =$ $[UO_2(L_X)]/([UO_2^{2^+}][L_X^{2^-}]))$ of $UO_2(L_X)$ (X = NH, O, S) in ethanol containing NEt₃ (0.4 mM), the spectral series of Fig. 3 were analyzed by HypSpec program.³⁰ As a result, $\log \beta_X$ of UO₂(L_X) for X = NH, O, and S are estimated to be 10 ± 1 , 7.24 \pm 0.02, and 5.2 \pm 0.1, respectively. Since all the coordinating atoms except for X are common in the studied systems, the difference in $\log \beta_{\rm x}$ observed here can be ascribed to the difference in affinity of X with UO₂²⁺. As widely-accepted in the HSAB principle, the hardness of X atoms follows $O > NH > S.^{14,15}$ However, $\log \beta_X$ of $UO_2(L_X)$ decrease in the order of $UO_2(L_{NH}) > UO_2(L_O) > UO_2(L_S)$, which is difficult to be rationalized only by the HSAB principle. To understand this trend, we focus on difference in basicity of X in L_x^{2-} . The pK_a values of protonated diethylamine ((CH₃- $CH_2_2NH_2^+$, dimethyl ether (($CH_3_2OH^+$), and dimethyl thioether ($(CH_3)_2SH^+$) are 11.0 (ref. 48), -3.8 (ref. 48), and -5.4 (ref. 48), respectively, which is exactly in line with the order of $\log \beta_x$



Fig. 3 UV-vis absorption spectra of the ethanol solutions of (a) L_{NH}^{2-} , (b) L_{O}^{2-} and (c) L_{S}^{2-} at different total UO_{2}^{2+} concentrations under the presence of 0.4 mM NEt₃. Total concentration of L_{X}^{2-} : 0.1 mM. Black and red lines are spectra of $C_U/C_L = 0$ and 1.0, respectively. Insets: plots of absorbance at 370 nm with an increase in C_U/C_L .

of $UO_2(L_x)$ described above. Therefore, the basicity of X atom would also provide some contribution to the thermodynamic stability of $UO_2(L_x)$. At this moment, it is still too early to verify linear free energy relationship between log β_x and pK_a .

To further elucidate the nature of U–X bonds in $UO_2(L_X)$, we carried out DFT calculations of $UO_2(L_X)$, followed by the natural bond orbital (NBO) analysis. The molecular structures of $UO_2(L_X)$ were taken from those of $UO_2(L_X)$ determined by X-ray crystallography, and were optimized with B3LYP method.³² The optimized structures of $UO_2(L_X)$ are shown in Fig. S4,† and selected bond lengths are summarized in Table S2.† All the bond distances well agree with those determined crystallographically (Table 1). Table S3† summarizes natural charges and Wiberg bond indices (WBI)^{17,18,40} of center U and coordinating atoms in the optimized structures.

No significant differences were found in the natural charge on the axial and equatorial coordinating atoms except for X. Both N(3) in $UO_2(L_{NH})$ (-0.646) and O(5) in $UO_2(L_0)$ (-0.565) have negative natural charges, indicating that the center U and X atoms interact electrostatically. In contrast, the natural charge of S(1) in $UO_2(L_s)$ is positive (+0.326), implying that the electrostatic attraction between U and S is little expectable despite significant penetration between these atoms in $UO_2(L_s)$ within the sum of van der Waals radii as described above. To provide a rationale for the U-S bonding interaction experimentally observed, bond orders of U-X interactions were estimated in terms of WBI. As a result, some covalency was detected in the U-S bond of $UO_2(L_s)$ as pronounced by WBI = 0.471, which is significantly larger than those of the other U–X bonds (WBI = 0.277–0.345). Therefore, the bonding interaction between U and S of $UO_2(L_S)$ is rather covalent, while it is somewhat weakened by the electrostatic repulsion between these positively charged atoms. The significant covalency of the U-S interaction compared with the electrostatic characters in U-NH and U-O would be a typical manifestation of the HSAB principle. In connection with this, N is usually considered to be softer than O, while the stability of $UO_2(L_{NH})$ is greater than $UO_2(L_0)$ despite the hardness of $UO_2^{2^+}$. The stronger basicity of NH provides an additional effect to strengthen the U-NH bond compared with that of U-O.

Electrochemistry and spectroelectrochemistry of $UO_2(L_X)$ (X = NH, O, S)

As mentioned above, X strongly affects the thermodynamic stability of $UO_2(L_x)$. Recently, we have reported that the redox potential of $UO_2(R_1,R_2-^{Me}saldien)$ (Fig. 1(a)) is significantly governed by substitution at R_1 and R_2 positions. Therefore, we expect that the difference in X may also vary the redox potentials of $UO_2(L_x)$. To clarify this point, the electrochemical measurements of $UO_2(L_x)$ in DMSO were carried out. Fig. 4 shows the obtained cyclic voltammograms of $UO_2(L_x)$, where a couple of cathodic (E_{pc}) and anodic peaks (E_{pc}) has been observed. These redox waves are reproducible even in multiple scanned cyclic voltammograms recorded at the potential sweep rate (ν) of 100 mV s⁻¹, indicating that the reduction product at E_{pc} undergoes no successive reactions, and is fully reoxidized to $UO_2(L_x)$ at E_{pa} (Fig. S6†). The peak potential separation ($E_{pc} - D$)

 $E_{\rm pa}$) tends to increase (111–490 mV) with increasing v from 50 mV s^{-1} to 500 mV s^{-1} (Fig. S7 and Tables S4–S6[†]), implying that these redox systems of $UO_2(L_x)$ are quasireversible. Even after careful survey of the DFT calculations described later, we, however, could not find any critical rationales for the differences in the electrochemical reversibility of these systems. Anyway, the peak potential separations $(E_{pa} - E_{pc}, \text{ see Table S6 in ESI}^{\dagger})$ of $UO_2(L_s)$ were also much greater than the theoretical value of a reversible system (59 mV). Therefore, all the systems studied here are regarded to be electrochemically irreversible. Although we do not have unequivocal explanation for the above points at this moment, solvation structures around these uranyl complexes could be largely modified through the electron transfer. Note that all the redox reactions are chemically reversible as demonstrated by occurrence of the isosbestic points in the spectroelectrochemical experiments shown in Fig. 5, S8 and S9.† The diffusion coefficients (D_0) of $UO_2(L_{NH})$, $UO_2(L_0)$, and $UO_2(L_S)$



Fig. 4 Cyclic voltammograms for the redox couples of $UO_2(L_X)$ (X = NH, O, S) in DMSO at 295 K. Concentration of the complex was adjusted to 1 mM and tetra-*n*-butylammonium perchlorate (0.1 M) was used as a supporting electrolyte. Scan rates are 100 mV s⁻¹.



Fig. 5 UV-vis-NIR spectral change of electrochemical reduction of UO₂(L_o) recorded at different applied potentials from -1.475 V to -1.665 V vs. Fc^{0/+} (potential step: 0.015 V) in DMSO with 0.1 M TBAP at 295 K. Black and red bold curves represent absorption spectra of UO₂(L_o) and [UO₂(L_o)]⁻, respectively. Wavenumber regions: (a) 33 333–4500 cm⁻¹, (b) 20 000–4500 cm⁻¹. Inset: Nernstian plot calculated from absorbance at 24 630 cm⁻¹.

in these systems at 295 K were estimated as 1.6 \times 10 $^{-6}$, 1.8 \times 10^{-6} and 8.1×10^{-7} cm² s⁻¹, respectively, where the redox reactions observed in Fig. 4 were assumed to be electrochemically irreversible.49 As summarized in Tables S4-S6,† the formal potential $E^{\circ\prime}$ (=($E_{\rm pc} + E_{\rm pa}$)/2) of each UO₂(L_x) is around -1.60 V vs. $Fc^{0/+}$ with regardless of v, and also seems not to be largely affected by X. The $E^{\circ'}$ value of $UO_2(L_{NH})$ well agrees with that of its analogue, UO₂(tBu,MeO-^{Me}saldien), we reported previously $(-1.60 \text{ V} \text{ vs. Fc}^{0/+} \text{ in DMSO}).^{21,22}$ Therefore, the coordinating L_X^{2-} would not have strong contribution to the redox events of $UO_2(L_x)$. From these results, we assume that the redox centers of all $UO_2(L_x)$ are the UO_2^{2+} moiety. However, cyclic voltammograms does not provide any detailed information about the reductant of $UO_2(L_x)$. Hence, we carried out the spectroelectrochemical measurements and theoretical calculations to further understand the redox chemistry of $UO_2(L_x)$.

To determine the electron stoichiometry (*n*) in the reduction of $UO_2(L_x)$, the spectroelectrochemical measurements were performed. The UV-vis-NIR spectra of each system were recorded at different potentials (*E*). Fig. 5, S8 and S9† show the obtained spectral variations at X = O, NH, and S, respectively. As a general trend, the absorption bands of $UO_2(L_x)$ around 30 000 and 20 000 cm⁻¹ gradually decreased with decreasing *E*, while new absorption bands appeared around 25 000 and 15 000 cm⁻¹. Moreover, isosbestic points were clearly observed, indicating that the redox equilibria of $UO_2(L_x)$ only take place in the current potential ranges. Using the absorbance at 24 630 or 24 876 cm⁻¹, the concentration ratio (C_O/C_R) between the oxidant ($UO_2(L_x)$) and its reductant at each *E* was calculated. The relationship between C_O/C_R and *E* should follow the Nernstian equation, eqn (2).

$$E = E^{\circ'} + (RT/nF)\ln(C_{\rm O}/C_{\rm R})$$
⁽²⁾

where $E^{\circ'}$, R, T, and F are the formal potential, the gas constant (8.314 J mol⁻¹ K⁻¹), the absolute temperature, and the Faraday constant (96 485 C mol⁻¹), respectively. The slope and intercept of the linear relationship between E and $\ln(C_O/C_R)$ (insets of Fig. 5(b), S8(b) and S9(b)†) allow to determine n and $E^{\circ'}$ of the

redox reactions of $UO_2(L_x)$. The estimated *n* values of $UO_2(L_x)$ are close to unity (Table S7†), indicating that the reduction of $UO_2(L_x)$ affords $[UO_2(L_x)]^-$. The $E^{\circ\prime}$ values estimated from the spectroelectrochemical measurements (Table S7†) agree with those observed in the CV measurements (Tables S4–S6†).

UV-vis-NIR spectra of $UO_2(L_X)$ and $[UO_2(L_X)]^-$ in DMSO were summarized in Fig. 6. The spectral features of all $UO_2(L_X)$ are quite similar to each other. All $UO_2(L_X)$ showed characteristic bands around 28 000 and 24 000 cm⁻¹. These absorption bands were also observed in UO_2^{2+} complexes with Schiff base ligands, and can be assigned to the π - π * transition bands of Schiff base ligands.^{21,22} Therefore, the difference in X leads to no significant differences in the electronic structures of $UO_2(L_X)$.

Even after the reduction, $[UO_2(L_X)]^-$ with different X commonly have the intense bands at around 25 000 cm⁻¹ with ε $\sim 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ and weak bands at 16 400, 14 500, 12 200 and 7200 cm⁻¹ with $\varepsilon \sim 10^2 \text{ M}^{-1} \text{ cm}^{-1}$ (Fig. 6). Note that $[UO_2(L_{NH})]^{-1}$ has a characteristic band at 5200 cm⁻¹, although this absorption is not clearly observed in $[UO_2(L_0)]^-$ and $[UO_2(L_s)]^-$ (Fig. 6). The absorption bands at around 25 000, 16 400, 14 500, 12 200 and 7200 cm⁻¹ are generally observed in U^VO₂⁺ complexes with Schiff base ligands as reported previously.^{21,22} The intense absorption at 25 000 cm⁻¹ is assigned to a π - π * transition in the Schiff base ligands and/or a ligand-to-metal charge transfer (LMCT).^{21,22} In accordance with TD-DFT calculation,^{21,22} the absorption band at 16 400 cm⁻¹ is attributable to a metal-toligand charge transfer (MLCT) from a $5f\delta_u$ orbital of the U⁵⁺ center to the π^* orbital of the coordinating ligand. Finally, those at 14 500, 12 200 and 7200 cm^{-1} are ascribed to the f-f transitions arising from the 5f¹ electron configuration of U⁵⁺.^{21,22,35} $[UO_2(L_{NH})]^-$ only exhibited the absorption band at 5200 cm⁻¹ attributable to another f-f transition,^{21,22,35} while this is not the case for the others studied here. As a matter of fact, this transition is not always clearly observable as we reported previously.²² To theoretically support occurrence of U^VO₂⁺ in each $[UO_2(L_x)]^-$, we further performed DFT calculations of $[UO_2(L_X)]^-$.

Initially, the molecular structures of $[UO_2(L_X)]^-$ in DMSO were taken from those of $UO_2(L_X)$ determined by the X-ray



Fig. 6 UV-vis-NIR spectrum of $UO_2(L_X)$ (black) and one-electron reduced complexes $[UO_2(L_X)]^-$ (red) in DMSO containing 0.1 M tetra-*n*-butylammonium perchlorate at 295 K. $[UO_2(L_{NH})]^{-/0}$ (a), $[UO_2(L_O)]^{-/0}$ (b) and $[UO_2(L_S)]^{-/0}$ (c). Inset: expended views of NIR region.



Fig. 7 Spin-density plots of $[UO_2(L_{NH})]^-$ (a), $[UO_2(L_0)]^-$ (b), $[UO_2(L_S)]^-$ (c). Spin density values of U atom are 1.09 for $[UO_2(L_{NH})]^-$, 1.09 for $[UO_2(L_O)]^-$, 1.12 for $[UO_2(L_S)]^-$.

crystal structure and were optimized after addition of a single negative charge and doublet spin degeneracy to assume the one-electron reduction. The optimized structures of $[UO_2(L_X)]^-$ were shown in Fig. S10[†] and the selected structural parameters are summarized in Table S2.[†]

The U \equiv O_{ax} bond lengths of [UO₂(L_x)]⁻ are 1.86 Å, which are *ca.* 0.08 Å longer than those of the corresponding UO₂(L_x) determined by SCXRD (Table 1). These U \equiv O_{ax} bond lengths are very similar to those of the U^VO₂⁺ complexes with bis(phenolate) ligands (1.851(7)–1.868(8) Å).⁵⁰ The U–O bond lengths between U atom and phenolic O of [UO₂(L_x)]⁻ are *ca.* 0.15 Å longer than those of the corresponding UO₂(L_x) (Table 1). These U–O bond elongations indicate that these bond strengths are weakened by a decrease in the positive charge of U through the reduction from U^{VI}O₂²⁺ to U^VO₂⁺. Actually, an unpaired electron of [UO₂(L_x)]⁻ is exclusively localized in the center U as shown in the Mulliken spin density surfaces (Fig. 7), clearly indicating that these reduced complexes are of U^VO₂⁺ regardless of difference in X. Consequently, the X moiety does not largely affect the redox chemistry of [UO₂(L_x)]^{-/0}.

Conclusions

In this study, $UO_2(tBu, MeO-saldien-X)$ ($UO_2(L_X)$; X = NH, O, S) were synthesized and structurally characterized to discuss impacts of the heteroatoms (X) to the coordination chemistry of UO_2^{2+} . The crystal structures of $UO_2(L_X)$ showed the fivecoordinated UO_2^{2+} with L_X^{2-} in the equatorial plane. The $U \equiv O_{ax}$ bond length of UO_2^{2+} and the bond length between U and phenolic O are not affected by the difference in X. On the other hand, the U-X bond length increases in the order of $UO_2(L_0) <$ $UO_2(L_{NH}) < UO_2(L_S)$. After taking into account the differences in the atomic size of X, the normalized U-X bond strength in $UO_2(L_x)$ was found to follow U–O \approx U–NH > U–S. While the U–O and U-NH bond strengths are similar to each other, the weaker U-S interaction can be explained by the HSAB principle. The logarithmic conditional stability constant (log β_x) of UO₂(L_x) in ethanol containing 0.4 mM NEt₃ decreases in the order of $UO_2(L_{NH})$ (log $\beta_{NH} = 10$) > $UO_2(L_0)$ (log $\beta_O = 7.24$) > $UO_2(L_s)$ (log $\beta_{\rm S} = 5.2$). This trend cannot be explained only by the HSAB principle, but rather follows the order of basicity of X. The theoretical calculations of $UO_2(L_x)$ suggested that the ionic character of U-X bonds decreases in the order of U-NH > U-O > U-S. In contrast, the covalency increases as U-O < U-NH < U-S.

No significant differences were found in the electrochemistry of $UO_2(L_x)$ with different X in terms of $E^{\circ'}$ and U-centered redox reaction. As demonstrated in this work, a $UO_2^{2^+}$ -ligand bond strength does not always follow the HSAB principle, but is also affected by other factors such as Lewis basicity and balance between ionic and covalent interactions of donating atoms to the center metal. These points should be more carefully considered to design molecular structures of ligands suitable for hydrometallurgical separations of metal ions of interest.

Author contributions

T. T. devised the main conceptual ideas, carried out all experiments, and wrote the manuscript in consultation with K. T. K. T. supervised this project, discussed all experimental results with T. T., and edited the manuscript. All authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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