Hydroxy- and alkoxy-bridged dinuclear uranyl–Schiff base complexes: hydrolysis, transamination and extraction studies†

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The reaction of uranyl nitrate with 1,3-bis(salicylideneamino)-2-propanol (H_3L1) and 1,3-bis(3,5-di-*tert*-butylsalicylideneamino)-2-propanol (H_3L2) in the presence of triethylamine (Et_3N) yielded hydroxy- and alkoxy-bridged dinuclear complexes; $[(UO_2)_2(L1)(OH)(MeOH)_2]\cdot(MeOH)_2$ (**1**·$(MeOH)_2$) and $[(UO_2)_2(L2)(OH)(MeOH)_2]\cdot(MeOH)_2$ (**2**·$(MeOH)_2$). The crystal structures of **1**·$(DMF)_2$ and **2**·$(DMF)_2$ exhibit an unsymmetrical central U_2O_2 core involving bridging alkoxy- and hydroxy-oxygen atoms. The geometry around the uranium center in **1**·$(DMF)_2$ and **2**·$(DMF)_2$ is that of a distorted pentagonal bipyramid with the solvent molecule occupying the fifth coordination site. The flexible nature of the ligand backbone is more pronounced in **2**·$(DMF)_2$ compared to **1**·$(DMF)_2$, yielding two molecules per unit cell in different conformations. Under similar reaction conditions, using ethylenediamine as a base, the respective Salen-based uranyl compounds, $[UO_2(Salen)(MeOH)]$ (**3**) and $[UO_2(Bu^t_2\text{-Salen})(MeOH)]$ (**4**) are obtained due to transamination of the ligand backbone. Complexes **1**·$(MeOH)_2$ and **2**·$(MeOH)_2$ when reacted with an excess of ethylenediamine failed to yield the respective Salen-based complexes, **3** and **4**, respectively. The new compounds have been characterized using solution (NMR and UV-Vis) and solid-state (IR, X-ray crystallography) techniques. Hydrolysis of **1**·$(MeOH)_2$ and **2**·$(MeOH)_2$ in the pH range 1–14 was studied using UV-Vis spectroscopy and compared with the hydrolysis of **3** and $[UO_2(Salophen)(MeOH)]$ (**5**). A two-phase extraction study suggests quantitative removal of uranyl ions from the aqueous phase at higher pH conditions.

Introduction

Actinide coordination chemistry has attracted attention due to the development of nuclear technology for the production of electricity. The remediation of the resulting nuclear waste generated, in which uranium is a major contributor to the long-term radioactivity, is a primary concern.[1] However, the separation of actinides from lanthanides is difficult due to their similar oxidation states and ionic radii.[2] Various ligand systems have been used as extractants, including organic phosphorous oxides,[3] crown ethers, azacrowns, calixarenes and modified calixarenes,[4,5] hydroxamic acids,[6] and Schiff base ligands.[7,8] Macrocyclic ligands and calixarene compounds are either too rigid or too flexible for complexation and instead result in the formation of uranyl salts or polymeric arrays with weak interactions.[9,10] Schiff base (SB) ligands are potential candidates for selective separation as they contain multidentate mixed aza- and oxo-cores and possess sufficient steric freedom, while lacking the problems associated with macrocyclic cavity size. One drawback, however, is that Schiff base compounds are susceptible to hydrolysis and transamination by nucleophiles due to the presence of an imine group (C=N).[11] The role of the metal ion as catalyst in the hydrolysis and transamination of SB ligands, where the transamination reaction is equilibrium controlled, and the excess of exchanging amine favors the reaction, is well documented.[12,13] In a recent study, the uranyl ion has been demonstrated to catalyze the reversible transamination of 2-methylalanine with pyridoxal (Vitamin B_6) yielding $[(UO_2PmHpyr)_3(\mu_3\text{-}O)]Cl\cdot 3H_2O$ (PmHpyr = pyridoxaminylpiruvate anion).[14] Transamination in uranyl–SB complexes with 8-hydroxy-7-quinolinecarbaldehyde has also been reported, where the addition of either ethylenediamine or diaminobenzene yields symmetrical tetradentate SB complexes.[15]

In an effort to synthesize stable uranyl–SB complexes which could be used as model compounds in the investigation of new means of remediation of uranium from aqueous sources or nuclear wastes, we here report the synthesis of $[(UO_2)_2(L1)(OH)(MeOH)_2]\cdot(MeOH)_2$ (**1**·$(MeOH)_2$)[16] and $[(UO_2)_2(L2)(OH)(MeOH)_2]\cdot(MeOH)_2$ (**2**·$(MeOH)_2$), which do not undergo facile nucleophilic addition and/or substitution reactions. Hydrolysis of **1**·$(MeOH)_2$ and **2**·$(MeOH)_2$ in the pH range 1–14 are studied along with comparison with alkyl- and aryl-backbone containing uranyl–SB complexes, $[UO_2(Salen)(MeOH)]$ (**3**) (Salen = *N*,*N*′-ethylenebis(salicylidenimine)) and $[UO_2(Salophen)(MeOH)]$ (**5**) (Salophen = *N*,*N*′-Disalicylidene-*o*-phenylenediamine). Transamination reaction of $[UO_2(Salophen)(MeOH)]$ (**5**) and $[UO_2(Bu^t_2\text{-Salophen})(MeOH)]$ (**6**) is also reported for comparison with **1**·$(MeOH)_2$ and **2**·$(MeOH)_2$.

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† Electronic supplementary information (ESI) available: Packing diagrams of **1**·$(DMF)_2$ and **2**·$(DMF)_2$, extended tables for bond distances and angles, hydrolysis profile of H_3L2, **4** and **6**, UV-Vis profile for extraction at pH 5 using method A. CCDC reference numbers 656873 and 662434. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b800469b

Experimental

General procedure

$UO_2(NO_3)_2{\cdot}6H_2O$, 1,3-diamino-2-propanol, salicylaldehyde and 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde were purchased from Acros and used as received. The ^1H and ^{13}C NMR were recorded on a Bruker AV 400 spectrometer operated at 400 MHz with d_6-DMSO as the solvent with tetramethylsilane as the reference. All melting points were recorded on a Mel-temp II melting point apparatus, and the values are uncorrected. The IR data were recorded as KBr pellets on SHIMADZU Inc. IR, Prestige-21 Fourier Transform Infrared Spectrophotometer in the range 400–4000 cm^{-1}. Electrospray ionization mass spectrometry was performed on a Micromass QTOF mass spectrometer (Waters Corp, Milford MA). All UV data was collected using a Cary 50 UV-Vis spectrophotometer with a xenon lamp in the range 200–1200 nm.

X-Ray crystallography

Crystals of **1**·$(DMF)_2$ and **2**·$(DMF)_2$ were obtained in good yield by slow evaporation of the precipitates dissolved in DMF at room temperature. Quality crystals could also be obtained from d_6-DMSO as **1**·$(DMSO)_2$ and **2**·$(DMSO)_2$. X-Ray diffraction data were collected at −80 °C on a Bruker SMART APEX CCD X-ray diffractometer unit using Mo-Kα radiation from crystals mounted in Paratone-N oil on glass fibers. SMART (v 5.624) was used for preliminary determination of cell constants and data collection control. Determination of integrated intensities and global cell refinement were performed with the Bruker SAINT Software package using a narrow-frame integration algorithm. Refinement was performed against F^2 by weighted full-matrix least square, and empirical absorption corrections (SADABS)[17] were applied. The program suite SHELXTL (v 5.1) was used for space group determination, structure solution, and refinement.[18] Hydrogen atoms were placed at calculated positions using suitable riding models with isotropic displacement parameters derived from their carrier atoms. The *tert*-butyl groups on molecule **2b** were disordered over two positions (60 and 40%) and restraints were applied to make chemically equivalent bonds approximately equal in the disordered fragments. Crystal data, selected bond distances and angles, are provided in Tables 1–3.

CCDC reference numbers 656873 and 662434.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b800469b

Extraction and hydrolysis studies

Two-phase extraction studies ($CHCl_3/H_2O$) were performed to determine the extraction capability for the removal of UO_2^{2+} ion from aqueous solution. The ligand H_3L2, quantitatively soluble in chloroform, was used for extraction studies. Fresh solutions of $UO_2(NO_3)_2{\cdot}6H_2O$ were prepared in DI water, and the pH was adjusted with HNO_3 and KOH (± 0.05). Two different methods were employed for studying extraction.

Method A (exposure time): 5 mL of aqueous UO_2^{2+} solution (4 mM) was added to the 5 mL of organic phase containing H_3L2 (8 mM) in scintillation vials and shaken for 20 s. The absorption spectra of the aqueous phase were determined at 1–8 h.

Table 1 Crystal data for **1**·$(DMF)_2$ and **2**·$(DMF)_2$ (refinement method: full-matrix least squares on F^2)

	1·$(DMF)_2$	**2**·$(DMF)_2$
Empirical formula	$C_{23}H_{30}N_4O_{10}U_2$	$C_{87}H_{143}N_{11}O_{23}U_4$
M_r	998.57	2663.240
λ/Å	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a/Å	11.797(3)	16.636(2)
b/Å	9.784(2)	16.641(2)
c/Å	24.594(5)	20.421(3)
α/°	90.00	104.963(3)
β/°	94.811(4)	93.128(3)
γ/°	90.00	103.839(3)
V/Å^3	2828.7(1)	5262.2(1)
Z	4	2
D_c/Mg m^{-3}	2.345	1.682
μ/mm^{-1}	11.495	6.205
$F(000)$	1840	2588
Crystal size/mm	0.1 × 0.1 × 0.05	0.1 × 0.5 × 0.05
Reflns collected	18601	36319
Indep. reflns	4058	15175
R_{int}	0.0687	0.1222
GOF of F^2	0.858	0.868
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0272$, $wR_2 = 0.0539$	$R_1 = 0.0451$, $wR_2 = 0.901$
R indices (all data)	$R_1 = 0.0364$, $wR_2 = 0.0557$	$R_1 = 0.0686$, $wR_2 = 0.967$
$\Delta\rho_{max,min}$/e Å^{-3}	1.177, −0.691	1.811, −1.632

Table 2 Selected bond distances (Å) and angles (°) for **1**·$(DMF)_2$

U1–O1	1.792(4)	U1–O2	1.783(4)
U1–O6	2.241(5)	U1–O7	2.380(5)
U1–O8	2.327(4)	U1–N1	2.544(5)
U2–O3	1.778(4)	U2–O4	1.794(4)
U2–O5	2.235(5)	U2–O7	2.364(4)
U2–O8	2.343(4)	U2–N2	2.579(5)
U2–O1D1	2.400(5)	U1–O1D2	2.461(4)
U1–U2	3.8693(8)		
O1–U1–O2	178.7(2)	O1–U1–O6	90.76(2)
O2–U1–O8	91.90(2)	O6–U1–O8	154.81(2)
O7–U1–O8	68.84(2)	O3–U2–O4	179.5(2)

Furthermore, separate vials containing organic solvent without H_3L2 and 5 mL of aqueous UO_2^{2+} solution at the respective pH were prepared for blanks.

Method B (sequential extraction): Organic phase containing 20 mL of H_3L2 (4 mM) and triphenylphosphine oxide (TPPO, 6 mM) was added to 20 mL of aqueous UO_2^{2+} (3 mM) solution and shaken in a separating funnel and the organic layer was removed. The aqueous layer was checked for uranyl concentration by UV-Vis. To the aqueous phase an equivalent amount of fresh organic solvent containing H_3L2 (4 mM) and TPPO (6 mM) was added again and the process was repeated until no UO_2^{2+} peak was observed in the UV-Vis spectrum of the aqueous phase. The blank for this method consists of extraction of 5 mL of UO_2^{2+} (3 mM) with 5 mL of TPPO (6 mM) dissolved in $CHCl_3$. The calculations for the reduction of uranyl ion from the aqueous media were done based on the band observed for UO_2^{2+} at *ca.* 420 nm.[19]

For hydrolysis studies, stock solutions of **1**·$(MeOH)_2$, **3** and **5** (0.1 mM each) were prepared by dissolving the respective compound in 95 : 5 $CHCl_3$–MeOH solution (100 mL each), whereas a stock solution of **2**·$(MeOH)_2$ (0.1 mM) was prepared

Table 3 Selected bond distances (Å) and angles (°) for **2**·(DMF)$_2$

2a			
U1–O1	1.762(6)	U1–O2	1.785(6)
U1–O5	2.221(6)	U1–O6	2.383(6)
U1–O8	2.389(6)	U1–N1	2.541(7)
U2–O3	1.766(6)	U2–O4	1.776(6)
U2–O6	2.341(6)	U2–O7	2.254(6)
U2–O8	2.375(6)	U2–N2	2.558(7)
U1–U2	3.9340(7)		
O1–U1–O2	179.0(3)	O1–U1–O5	88.0(3)
O1–U1–O8	87.8(2)	O2–U1–O5	91.1(3)
O2–U1–O6	89.6(3)	O3–U2–O4	179.5(3)
O3–U2–O6	90.8(3)	O3–U2–O7	89.5(3)
O3–U2–O8	88.9(3)	O4–U2–O6	88.7(2)
O7–U2–O8	155.6(2)		
2b			
U3–O9	1.774(6)	U3–O10	1.767(6)
U3–O13	2.227(6)	U3–O14	2.392(6)
U3–O16	2.341(6)	U3–N3	2.549(7)
U4–O11	1.764(6)	U4–O12	1.796(6)
U4–O14	2.352(6)	U4–O15	2.239(6)
U4–O16	2.338(6)	U4–N4	2.561(7)
U3–U4	3.8470(6)		
O9–U3–O10	178.4(3)	O9–U3–O13	92.4(3)
O9–U3–O14	88.0(2)	O10–U3–O13	86.8(3)
O10–U3–O16	87.1(3)	O13–U3–O16	155.4(2)
O13–U3–O14	135.8(2)	O14–U3–O16	68.25(19)

in 100 mL of $CHCl_3$. An equivalent amount of aqueous solution at pH 1–14 was added to separate vials containing 5 mL of H_3L2 (3 mM), **1**·$(MeOH)_2$ (0.1 mM), **2**·$(MeOH)_2$ (0.1 mM), **3** (0.1 mM) or **5** (0.1 mM) in organic solvent and shaken for 60 s. The solution was left undisturbed overnight, and the organic layer was isolated for hydrolysis studies employing UV-Vis. The extent of hydrolysis at different pH was interpreted relative to the spectra at neutral pH.

Synthesis of Schiff bases and uranium complexes

The ligands were synthesized according to the literature methods.[20] Complexes **1**·$(MeOH)_2$ and **2**·$(MeOH)_2$ were synthesized by refluxing 50 mL of MeOH–$CHCl_3$ (50 : 50) solution containing respective ligands; H_3L1 (2 mmol, 0.6 g) and H_3L2 (2 mmol, 1.0 g), Et_3N (2 mmol, 0.2 g) and $UO_2(NO_3)_2$·$6H_2O$ (2 mmol, 1.0 g) for 5–6 h. Uranyl–Salen (**3** and **4**) and uranyl–Salophen (**5** and **6**) compounds were synthesized according to the literature methods.[21,22] The resulting precipitates obtained were filtered off, washed with 5 mL of cold MeOH–$CHCl_3$ (1 : 1) mixture and dried under vacuum.

$[(UO_2)_2(L1)(OH)(MeOH)_2]$·$(MeOH)_2$ (1·$(MeOH)_2$). Yield: (0.9 g, 98%), Mp >200 °C, δ_H (400 MHz, d_6-DMSO): 2.8 (12H, s, 2DMSO), 4.7, 4.9 and 5.8 (5H, m, CH_2–CH–CH_2), 6.7–7.9 (8H, m, $2C_6H_4$), 9.4 (2H, s, CHN), 11.7 (1H, s, OH). δ_C (400 MHz, d_6-DMSO): 31 and 36 (CH_2N), 71 (CHO), 115–163 (phenyl), 167 and 170 (CHN). λ_{max}(DMF)/nm: 270, 330, 385 (ε/dm^3 mol^{-1} cm^{-1} 2300, 1000 and 260). ν_{max}(KBr)/cm^{-1}: 2919, 1629, 1541, 1469, 1447, 1383, 1309, 1212, 1151, 1030, 895, 801. *m*/*z* (ESI): 980 (M^+ + 2MeOH) (10%).

$[UO_2(L2)(OH)(MeOH)_2]$·$(MeOH)_2$ (2·$(MeOH)_2$). Yield: (1.0 g, 87%), Mp >200 °C, δ_H (400 MHz, d_6-DMSO, ppm): 1.34 and 1.79 (18H, s, $C(CH_3)_3$), 3.17 (12H, s, 2DMSO), 4.6, 4.8 and 5.7 (5H, m, CH_2–CH–CH_2), 7.4 and 7.6 (4H, d, C_6H_2), 9.4 (2H, s, CHN), 12.5 (1H, s, 1H). δ_C (400 MHz, d_6-DMSO): 29, 31, 34 and 35 (−$C(CH_3)$), 46 (CH_2N), 63 (CHO), 118–158 (phenyl) and 169 (C=N). λ_{max}(DMF)/nm: 270, 350, 400 (ε/dm^3 mol^{-1} cm^{-1} 2100, 600 and 230). ν_{max}(KBr)/cm^{-1}: 2953, 1627, 1531, 1457, 1435, 1384, 1214, 1167, 876. *m*/*z* (ESI): 1203 (M + 2MeOH)$^+$ (100%).

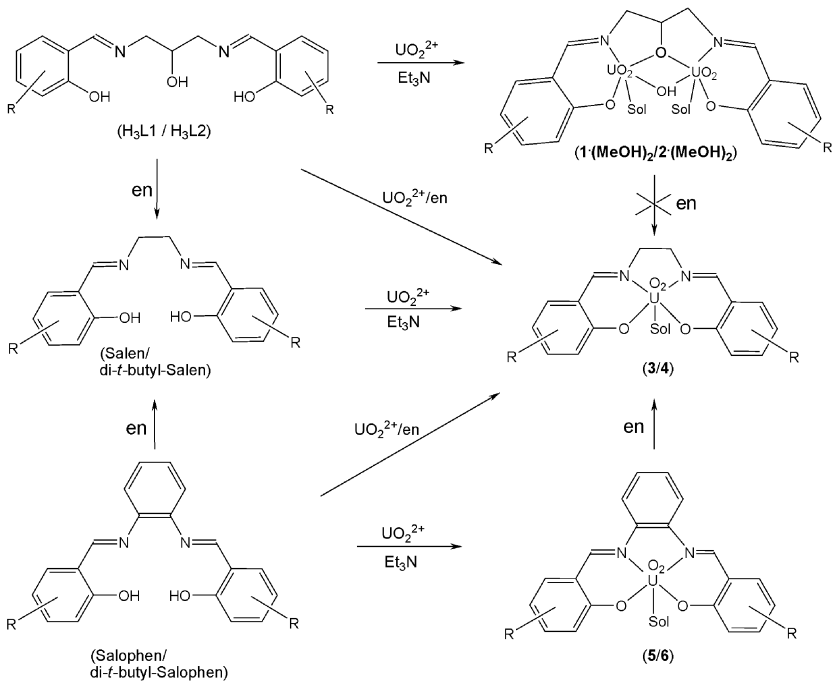
Transamination reactions

Ligands. Ligand (Salophen, Bu^t_2-Salophen, H_3L1 or H_3L2) (1 mmol) was dissolved in a minimal amount of MeOH–$CHCl_3$ (50 : 50), and to this, ethylenediamine (1–2 mmol) dissolved in methanol (2 mL) was added. The resulting solution was stirred overnight. The solvent was then removed to obtain a precipitate, which was washed with cold MeOH to obtain Salen or Bu^t_2-Salen. The ^{1}H NMR indicates formation of the respective compounds and agrees with the reported data.[21,22]

Uranyl-complexes. Compound **5** (1 mmol) was dissolved in a 50 : 50 mixture of MeOH–$CHCl_3$ (10 mL) and to this solution ethylenediamine (1–2 mmol) dissolved in minimum amount of MeOH was added and stirred overnight. The solvent was then removed to obtain a precipitate and washed with cold $CHCl_3$ to obtain **3**. Compound **6** under similar conditions does not yield **4**; however, the reaction proceeds to completion when heated to reflux. The precipitates were removed, washed with cold MeOH and dried under vacuum. Compound **1**·$(MeOH)_2$ or **2**·$(MeOH)_2$ (1 mmol) was dissolved in 50 : 50 MeOH–$CHCl_3$ mixture (10 mL) and to this ethylenediamine (3–4 mmol) was added, and the resulting mixture was refluxed for 2–3 h. The solvent was removed to obtain a precipitate, which was washed with cold MeOH–$CHCl_3$ (50 : 50) and dried under vacuum. ^{1}H NMR and crystallization from DMF indicates no transamination observed for **1**·$(MeOH)_2$ or **2**·$(MeOH)_2$.

Results and discussion

The ligands, H_3L1 and H_3L2 possess five potential donor atoms to complex with metal ions. The range of complex structures resulting from similar ligands reported in the literature varies from monomeric to polymeric controlled by varying the conditions of synthesis.[23,24] For instance, H_3L1 with transition-metal ions such as Cu^{2+}, Mn^{3+} and Zn^{2+} typically yields multinuclear (tri-, tetra- and hexanuclear) alkoxo-bridged clusters.[25–28] The uranyl complexes **1**·$(MeOH)_2$ and **2**·$(MeOH)_2$ were synthesized by heating to reflux an equivalent amount of ligand, uranyl nitrate hexahydrate and Et_3N in MeOH–$CHCl_3$ (50 : 50). Varying UO_2^{2+} : ligand ratio (1–3 stoichiometry) under similar reaction conditions only yielded **1**·$(MeOH)_2$ or **2**·$(MeOH)_2$. Using ethylenediamine as a base instead of Et_3N, compounds **3** and **4** were obtained. The catalytic role of uranyl ion in the transamination reaction, followed by the formation of **3** or **4** (something similar to the formation of $[(UO_2PmHpyr)_3(\mu_3\text{-}O)]Cl\cdot 3H_2O$)[14] can be ruled out because, in the absence of uranyl ion, ligands H_3L1 and H_3L2 undergo facile transamination with ethylenediamine to yield Salen and Bu^t_2-Salen, respectively. The diamine exchange is only observed when the exchanging amine is more basic than the amine used



Scheme 1 Scheme depicting the synthesis and transamination associated with ligands and uranyl complexes (R = H (**3** and **5**) and Bu^t_2 (**4** and **6**), sol = solvent, en = ethylenediamine).

to form the imine compound, in this case ethylenediamine replacing 1,3-diamino-2-propanol.[29] Under similar reaction conditions combination of ethylenediamine with **5** and **6** yields **3** and **4**, respectively, however, even with a three-fold excess of ethylenediamine, **1**·$(MeOH)_2$ and **2**·$(MeOH)_2$ do not undergo transamination (Scheme 1).

In the ^{1}H NMR, a significant shift in the ppm value of the imine HC=N bond is observed between free ligand (≈8.5 ppm) and uranium complexes (≈9.4 ppm) indicating the involvement of the lone pair on nitrogen with the metal center. A singlet over 11 ppm in both **1**·$(MeOH)_2$ and **2**·$(MeOH)_2$ indicates the presence of a bridging hydroxy group attached to the uranium center. In the IR spectra of the complexes, a strong peak around 1628 cm^{-1} compared to 1640 cm^{-1} of the free ligand indicates coordinated imine nitrogen.[30,31] Coordination through the phenolic hydroxy groups is shown by the shift in the C–O band for uranyl complex (1210 cm^{-1}) compared to the band observed for free ligands (1260 cm^{-1}).[32] The strong bands around 900 and 800 cm^{-1} represent the asymmetric and symmetric stretch of a linear uranyl moiety and are comparable to similar complexes.[32,33]

The UV-vis spectra for the free ligands and uranyl complexes in DMF are shown in Fig. 1. The absorption bands for ligands are observed around 270 and 320 nm (H_3L1) and 270 and 330 nm (H_3L2) arising from $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$, respectively. A red shift in the uranyl complexes is observed except for the band at 270 nm. The peak around 330 nm (**1**·$(DMF)_2$) and 350 nm (**2**·$(DMF)_2$) could be assigned to the LMCT transition of the imine group with appreciable red shift compared to the $n \rightarrow \pi^*$ of the free ligands.[15,32] Similar bands due to the imine coordination and LMCT (5f ← 2p oxygen) have been reported for uranyl complexes containing multidentate hydroxy groups (390 and 450 nm).[34]

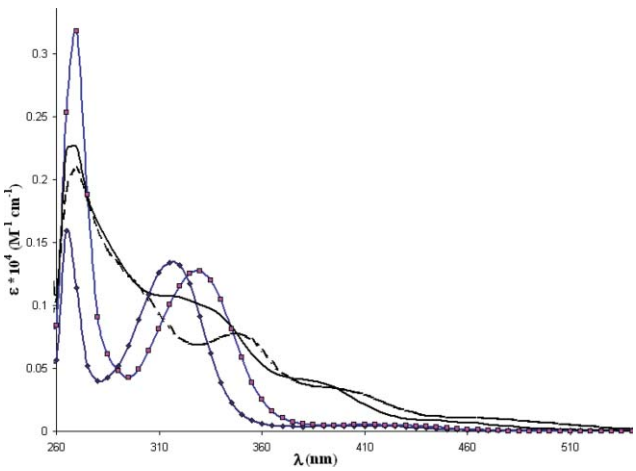


Fig. 1 Absorption spectra of ligands (0.25 mM) (H_3L1 = ◇; H_3L2 = □) and uranyl complexes (0.1 mM) (**1**·$(DMF)_2$ = —; **2**·$(DMF)_2$ = ---) in DMF.

The DMF adducts of **1** and **2** (Fig. 2 and 3 and Tables 2 and 3) were obtained from supersaturated DMF solutions containing the uranyl complexes. The crystal structure of **1**·$(DMF)_2$ has been described briefly earlier.[16] In the asymmetric unit of **2**·$(DMF)_2$, two molecules with different conformation and noticeable differences in the interatomic distances are observed (**2a** (boat) and **2b** (chair)). This might be due to the fluxional behavior of the *tert*-butyl groups present on the ligand backbone. The environment around the uranyl center is similar with equatorial phenolic oxygen, imine nitrogen, bridging alkoxy and hydroxy group along with the solvent molecules. The geometry around the uranium center is

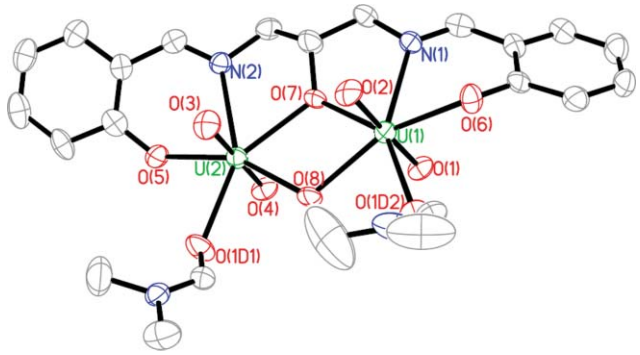


Fig. 2 Molecular structure of **1**·(DMF)$_2$ (ORTEP with 50% thermal ellipsoids). Hydrogen atoms are omitted for clarity.

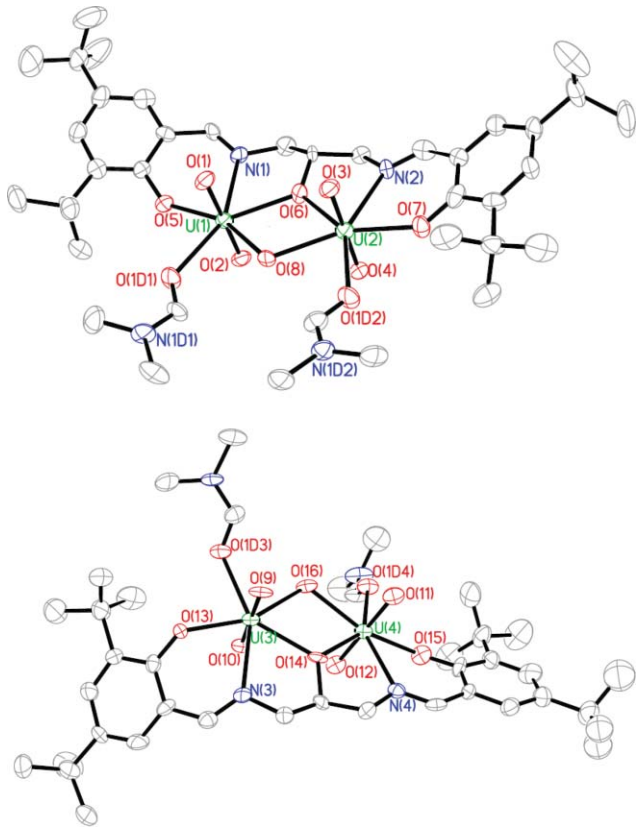


Fig. 3 Molecular structure of **2a** (top) and **2b** (bottom) with 50% thermal ellipsoids. Hydrogen atoms and solvent molecules are omitted for clarity.

best described as pentagonal-bipyramidal with axial O=U=O moiety. The U=O distances and O=U=O angles in **1**·(DMF)$_2$ (av. 1.78(4) Å; 178°) and **2**·(DMF)$_2$ (av. 1.77(6) Å; 178° (**2a**) and 1.77(6) Å); 179° (**2b**)) are typical of the corresponding distances and angles reported for similar uranyl compounds.[35]

The U–O_{phen} distances are unsymmetrical in both complexes with distances in the range 2.223(6)–2.253(6) Å, however, these are within the range observed in related complexes (2.231–2.296 Å).[34] The average U–N distances in **1**·(DMF)$_2$ (av. 2.561(5) Å) are slightly longer than those observed in **2**·(DMF)$_2$ (2.549(7) (**2a**) and 2.554(7) (**2b**) Å) and are typical of uranium nitrogen distances observed in uranyl–SB complexes (2.54–2.58 Å).[36,37]

The bridging alkoxy distances in **1**·(DMF)$_2$ (av. 2.372(4) Å) and **2**·(DMF)$_2$ (av. 2.362(6) (**2a**) and 2.372 (**2b**) Å) are in accordance with the U_{alkoxy} distances observed in [UO_2(Salophen)]$_2$ (2.387–2.463 Å)[38] and [(UO_2)(H_2L)$_2$(NO_3)$_2$] (2.360–2.389 Å)[39] (H_2L = aminoalcoholbis(phenolate)). In contrast, symmetrical distances have been reported for [Cu_2(L1)(μ–O_2CCH_2–C_6H_4–CH_2CO_2)]·2H_2O (1.944 Å).[40] The bridging hydroxy, U–O_{OH} distances in **1**·(DMF)$_2$ (av. 2.335(4) Å) and **2**·(DMF)$_2$ (2.375(6) (**2a**) and 2.330(6) (**2b**) Å) are unsymmetrical leading to the formation of an unsymmetrical central U_2O_2 core. The U–O_{OH} distances on an average are smaller than the U–O_{alkoxy} distances, indicating a stronger bond. The bridging hydroxyl distances are comparable with the corresponding distances observed in the uranyl–oxalate complex, [(UO_2)$_2$(C_2O_4)$_2$(OH)Na(H_2O)$_2$] (av. 2.287 Å);[41] uranyl–pyridine-2,6-dicarboxylato complex, [$HNEt_3$]$_2$[UO_2L_2]·2H_2O (2.319–2.357 Å);[42] as well as uranyl–inorganic structure such as [(UO_2)$_4$O(OH)$_6$]·5H_2O (2.303–2.433 Å).[43]

The interatomic U · · · U distances in **1**·(DMF)$_2$ (3.869(8) Å) and **2**·(DMF)$_2$ (3.847(6) (**2a**) and 3.933(7) (**2b**) Å) are too extended to be indicative of any metallic interactions.[38,44] These, however fall within the range of distances reported for dinuclear uranyl compounds (3.779–3.932 Å). The unsymmetrical distances in **1**·(DMF)$_2$ and **2**·(DMF)$_2$ could be attributed to the flexible nature of the ligand backbone, which is more pronounced in **2**·(DMF)$_2$. The distortion observed in the ligand backbone along the plane defined by the central U_2O_2 core is shown in Fig. 4. The phenyl groups are present on the same side of the U_2O_2 core in **2a** yielding a 'boat' conformation.

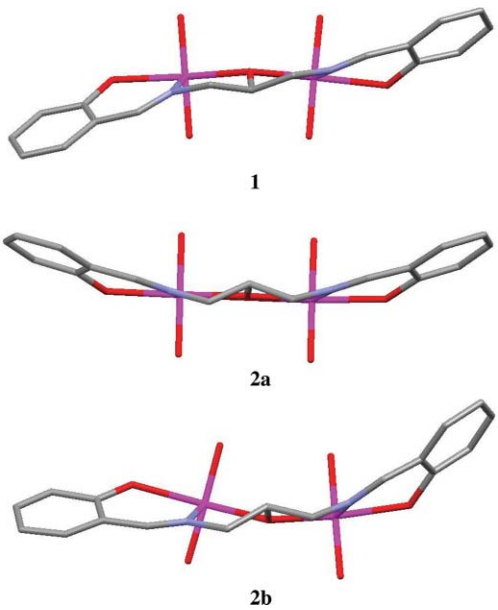


Fig. 4 Distortion observed in the backbone of **1**·(DMF)$_2$, **2a** and **2b**. The *tert*-butyl groups in **2a** and **2b** are omitted for clarity.[45]

Such a conformation has been reported for various mononuclear uranyl–SB complexes and attributed to the strong uranyl–ligand interaction, which forces the ligand to conform.[46] However, no correlation could be observed between bond distances, angles, and conformation of a few selected uranyl-complexes (Table 4). Such conformation is also reported for various transition metal–SB complexes including Cu^{2+}, Mn^{3+}, as well as U(IV)–SB

Table 4 Comparison of structural parameters of selected dinuclear uranyl–SB complexes. Average distances (Å) and angle ranges (°) are reported[a]

	Conform. (subst.)	U–O_{phenyl}	U–N	U–O_{bridge}	U···U	U_2O_2 core	Ref
1·$(DMF)_2$	c (H)	2.237	2.562	2.353	3.869	68.8–111.9	This work
2a	b (Bu^t)	2.237	2.548	2.369	3.934	67.2–112.7	This work
2b	c (Bu^t)	2.234	2.548	2.351	3.847	67.9–111.2	This work
$[UO_2(HL1)]_2$	b (H)	2.222	2.557	2.353	3.879	68.3–111.0	8
$[UO_2(HL2)]_2$	c (OH)	2.225	2.528	2.335	3.863	67.8–112.0	8
$[UO_2(HL3)]_2$	c (Bu^t)	2.232	2.562	2.358	3.925	67.8–112.9	8
$[UO_2(L4)]_2$	b (H)	2.225	2.527	2.441	3.876	69.4–106.3	38
$[UO_2(HL5)]_2$	c (H)	2.235	2.571	2.367	3.942	65.7–112.7	44

[a] c = chair; b = boat; L1/L2/L3 = 3-amino-1,2-propanediol based SB ligands; L4 = Salophen; L5 = SB derived from 4,6-*O*-ethylidene-β-D-glucopyranosylamine.

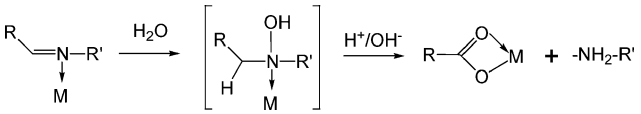
complexes.[40,47–79] In **1**·$(DMF)_2$ and **2b**, the phenyl groups are present on the opposite site of the U_2O_2 core with a chair conformation. In dinuclear uranyl–SB complexes containing 3-aminopropane-1,2-diol, a boat confirmation is observed in the backbone where phenyl groups contain no substituents. With substituents such as OH and *tert*-butyl groups, a chair conformation is observed, which was attributed to the electronic and steric effects. This is contrary to the conformations observed in **1**·$(DMF)_2$ and **2**·$(DMF)_2$. One possibility is that the conformation in the ligand backbone of a SB-complex is governed by crystal packing rather than steric or electronic effects.

Hydrolysis and extraction studies

The two-phase hydrolysis study of H_3L2 indicates that this ligand hydrolyzes in extreme pH conditions (pH 1, 2 and 13, 14; see ESI†). The hydrolysis profile of compounds **1**·$(MeOH)_2$, **2**·$(MeOH)_2$, **3** and **5** are shown in Fig. 5.

In the UV-Vis spectra of **1**·$(MeOH)_2$, a slight change in the λ_{max}(LMCT) is observed for bands at pH 1–3 (330 nm) compared to that observed at pH 7.0 (315 nm). A significant change in the spectra is observed at pH 12 and the characteristic peak around 315 nm is absent at pH 13 and 14. In **2**·$(MeOH)_2$, a profound shift in the λ_{max} is observed at pH 1–3. In compound **3**, the λ_{max}(340 nm) for pH 10–14 is not observed and a meagre shift at pH 1–3 is observed. On the other hand, for **5**, a significant shift in the λ_{max} is observed at pH 1, 2 and 11 and no peak is observed at pH 12–14. Compounds, **1**·$(MeOH)_2$ and **2**·$(MeOH)_2$ are stable in a much broader pH range and hydrolyze at extreme conditions. Kinetics and mechanism studies of the hydrolysis of imine have been studied extensively with the intermediacy of carbinolamines [–NH–CH(OH)–] formed by addition of a water molecule across imine and cleavage of the C–N bond in the N-protonated form.[50,51] It is likely that the hydrolysis of these complexes would follow the same mechanism (Scheme 2) with the formation of a carbinolamine intermediate followed by the formation of [UO_2(salicylic acid)](NO_3) and free amine. A characteristic peak for LMCT is not observed for [UO_2(salicylic acid)](NO_3) at high pH conditions in **1**·$(MeOH)_2$, **3** and **5**. Previously, we have reported that the hydrolyzed product of {[UO_2(3-(2-hydroxybenzylideneamino)propane-1,2-diol)]$_2$} in the presence of Ag(NO_3) yields [UO_2(salicylate)](Et_3NH).[8]

The attack of water or hydroxide ion on the protonated SB complex are the rate determining steps in acidic and basic conditions, respectively.[53] The formation of a carbinolamine intermediate in



Scheme 2 Scheme depicting hydrolysis of imine of metal–Schiff base complexes.[52]

1·$(MeOH)_2$ is indicated by the shift in λ_{max} at pH 1–3; however, complete breakdown of the complex is observed at pH 12–14. In contrast, for complex **2**·$(MeOH)_2$ formation of the carbinolamine intermediate is observed at pH 1–3. It is interesting to observe that at high pH conditions complex **2**·$(MeOH)_2$ appears to remain intact. This could only be explained due to its extreme solubility in the organic phase ($CHCl_3$) (Experimental section) compared to **1**·$(MeOH)_2$, **3** and **5**, which required a minimum amount of MeOH for complete dissolution.

Similar shifts in the λ_{max} peaks in the hydrolysis profile have been reported for the Ni^{2+}–2,2′-dipyridylmethylideneaniline complex, where metal ion stabilization of SB toward hydrolysis is reported.[52] Protection by the metal ion of the protonation of the imine nitrogen retards the breakdown of the intermediate leading to overall inhibition of the hydrolysis of the SB complex. The rate of hydrolysis of the SB-complex is related to the metal ion electron withdrawing abilities from the reaction center (imine bond).[53] It can be postulated that the stronger U–N interaction leading to the shorter imine bonds in **1**·$(DMF)_2$ (av. 1.279(8) Å) and **2**·$(DMF)_2$ (av. 1.274(1) Å) compared to **3** (av. 1.284 Å) and **5** (coordinating solvent = MeOH (1.289 Å); DMF (1.289 Å) and DMSO (1.290 Å)) might explain the robust nature of these complexes toward hydrolysis. Some macrocyclic complexes retain their imine bonds in water due to the "macrocyclic effect", but still are susceptible to intramolecular transamination reactions.[54,55] Comparing **1**·$(MeOH)_2$ and **2**·$(MeOH)_2$ with **5** and **6**, which easily undergo transamination, it can be inferred that the presence of the bridging alkoxy and hydroxy oxygen in the former compounds provides additional stability to the complexes.

The two-phase extraction studies reported here (Fig. 6) are studied at pH 5.0 only since H_3L2 hydrolyzes in the acidic region, and it was determined that extractions with SB are more effective at higher pH conditions.[7] Employing 'method A', extraction of uranyl ion from aqueous phase alone with H_3L2 dissolved in $CHCl_3$ indicates 40% reduction of uranyl concentration at pH 5.0. Only the first extraction is effective as UV-Vis indicates an increase of uranyl ion peak with time. This might be due to the formation of **2**·$(H_2O)_2$ in the aqueous phase, whose

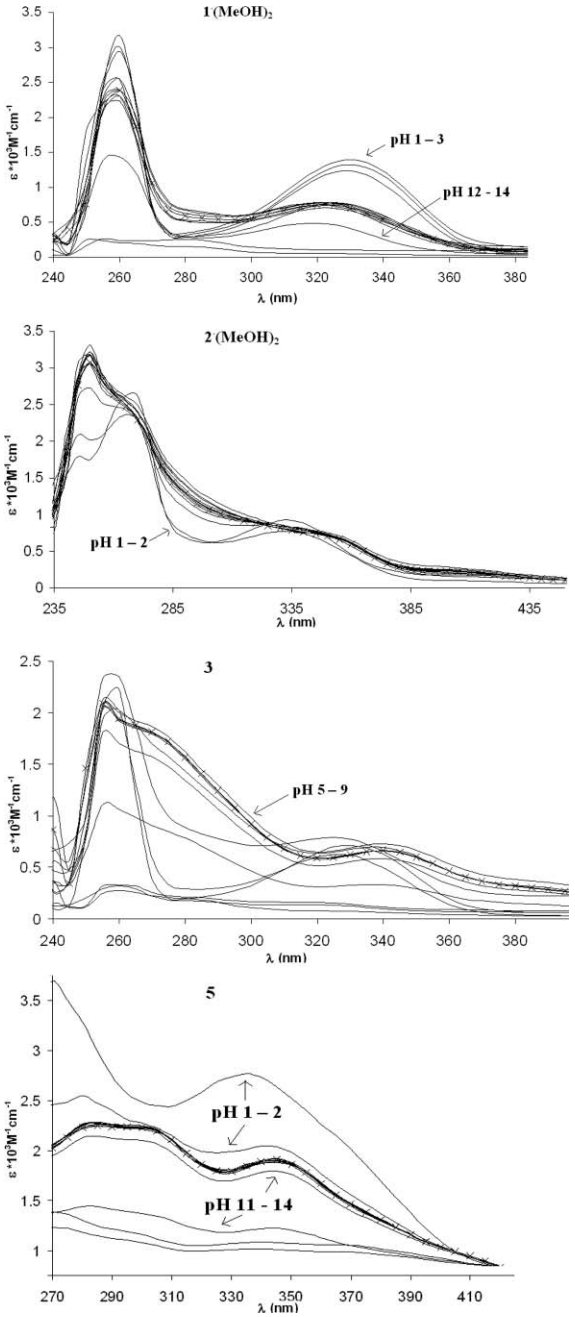


Fig. 5 Absorption spectra showing hydrolysis of **1**·$(MeOH)_2$, **2**·$(MeOH)_2$, **3** and **5** between pH 1–14. The bands indicated by × correspond to spectra at neutral condition.

solubility is further enhanced by the formation of an extended hydrogen bonding network.[56] Increasing the concentration of the ligand and the quantity of Et_3N did not affect the extraction results. The formation of **2**·$(H_2O)_2$ could be avoided by the use of a neutral ligand such as TPPO, which yields **2**·$(TPPO)_2$. A sequential extraction method (method B) was employed to avoid the equilibrium between **2**·$(TPPO)_2$ and **2**·$(H_2O)_2$. In this process a solution of H_3L2 and TPPO dissolved in $CHCl_3$ was shaken with uranyl solution (pH 5.0), and the organic layer was subsequently removed. The process was repeated with fresh organic solution containing both H_3L2 and TPPO. After four stages of extraction,

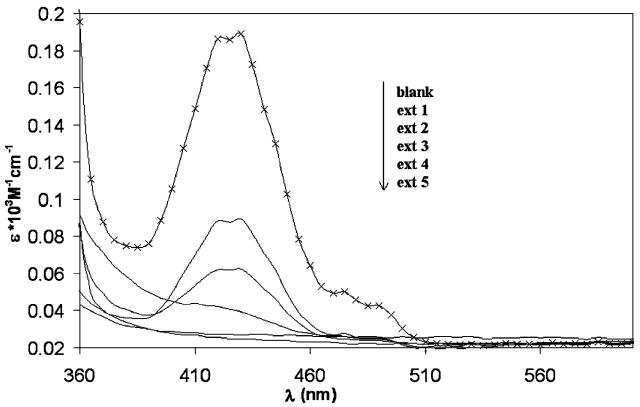


Fig. 6 UV-Vis profile for two-phase extraction of uranyl ion from aqueous phase at pH 5.0 employing a sequential extraction method (blank = ×).

absence of the characteristic peak of uranyl at 420 nm indicates complete removal of UO_2^{2+} ions from aqueous phase.

Conclusions

Novel uranyl compounds with extended chelation are fully characterized and their reactivity (transamination and hydrolysis) is reported. The compounds are similar with pentagonal bipyramidal geometry around the uranium atom and a central U_2O_2 core. Under experimental conditions compounds **1**·$(MeOH)_2$ and **2**·$(MeOH)_2$ do not undergo nucleophilic addition (hydrolysis) and substitution reaction (transamination). The hydrolysis of **1**·$(MeOH)_2$ or **2**·$(MeOH)_2$ compared to **3** and **5** indicates the robust nature of the backbone of the former in basic conditions. This could be due to the stronger C=N bonds and an additional stability provided by the bridging alkoxy and hydroxy groups. Such compounds could be useful to further explore the uranyl–SB chemistry toward understanding remediation and speciation, or for the use to stabilize wastes from nuclear fuel sources stored in alkaline conditions.

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Notes and references

1 J. Bruno and R. C. Ewing, *Elements.*, 2007, **2**, 343.
2 K. L. Nash, *Solvent Extr. Ion Exch.*, 1993, **11**, 729.
3 P. D. Wilson, *Nuclear Fuel Cycle: From Ore to Waste*, Oxford Science Publications, Oxford, UK, 1996.
4 P. D. Beer, G. D. Brindley, D. O. Fox, A. Grieve, M. I. Ogden, F. Szeme and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, 2002, 3101.
5 P. Thurey, N. Keller, M. Lance, J. D. Vigner and M. Nierlich, *New J. Chem.*, 1995, **19**, 619.
6 B. Saha, K. A. Venkatesan, R. Natarajan, M. P. Anthony and P. R. V. Rao, *Radiochim. Acta*, 2002, **90**, 455.
7 S. K. Sahu and V. Chakravortty, *J. Radioanal. Nucl. Chem.*, 1998, **227**, 163.
8 M. S. Bharara, K. Strawbridge, J. Z. Vilsek, T. H. Bray and A. E. V. Gorden, *Inorg. Chem.*, 2007, **46**, 8309.
9 M. Nierlich, J. M. Sabattie, N. Keller and J. D. Vigner, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1994, **50**, 52.

10 E. M. Holt, N. M. Alcock, R. R. Hendrixson, G. D. Malpass, R. G. Ghirardelli and R. A. Palmar, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1981, **37**, 1080.
11 M. I. D. Holanda, P. Krumholz and H. L. Chum, *Inorg. Chem.*, 1976, **15**, 890.
12 R. H. Holm, G. W. Everett and A. Chakravotry, *Prog. Inorg. Chem.*, 1966, **7**, 83.
13 R. K. Kohli and P. K. Bhattacharya, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 2872.
14 D. F. Back, G. M. de Oliveira and E. S. Lang, *Z. Anorg. Allg. Chem.*, 2007, **633**, 729.
15 A. T. Mubarak, *Spectrochim. Acta, Part A*, 2006, **65**, 1197.
16 M. S. Bharara, S. Tonks and A. E. V. Gorden, *Chem. Commun.*, 2007, 4006.
17 G. M. Sheldrick, *SADABS*, An empirical absorption correction program, Bruker Analytical X-Ray System, Madison, WI, 1996.
18 G. M. Sheldrick, *SHELXTL PC*, version 6.12, An integrated system for solving, refining, and displaying crystal structures from diffraction data, Siemens Analytical X-Ray Instruments, Inc, Madison, WI, 2001.
19 M. Glorius and G. Bernhard, *Radiochim. Acta*, 2007, **95**, 151.
20 V. V. Lukov, V. A. Kogan, V. M. Novotortsev, Y. P. Tupolova and I. E. Gevorkyan, *Koord. Khim.*, 2005, **31**, 376.
21 S. J. Gruber, C. M. Harris and E. Sinn, *Inorg. Chem.*, 1968, **7**, 268.
22 M. Green, J. Smith and P. A. Tasker, *Inorg. Chim. Acta*, 1971, **109**, 185.
23 J. A. Bondies, M. J. Maroney and V. L. Pecoraro, *Inorg. Chem.*, 1989, **28**, 2044.
24 G. D. Fallon, A. Markiewich, K. S. Murray and T. Quach, *J. Chem. Soc., Chem. Commun.*, 1991, 198.
25 R. Bagai, K. A. Abboud and G. Christou, *Dalton Trans.*, 2006, 3306.
26 A. Mukherjee, R. Raghunathan, M. K. Saha, M. Nethaji, S. Ramasesha and A. R. Chakravatry, *Chem.–Eur. J.*, 2005, **11**, 3087.
27 Y. Song, C. Massera, O. Roubeau, P. Gamez, A. M. M. Lanfredi and J. Reedijk, *Inorg. Chem.*, 2004, **43**, 6842.
28 S. Uhlenbrock, R. Weger and B. Krebs, *J. Chem. Soc., Dalton Trans.*, 1996, 3731.
29 L. G. Armstrong and L. F. Lindoy, *Inorg. Chem.*, 1975, **14**, 1322.
30 R. Kannappan, D. M. Tooke, A. L. Spek and J. Reedijk, *Inorg. Chim. Acta*, 2006, **359**, 334.
31 U. Casellato, S. Tamburini, P. Tomasin and P. A. Vigato, *Inorg. Chim. Acta*, 2002, **341**, 118.
32 A. A. A. Abu-Hussen, *J. Coord. Chem.*, 2006, **59**, 157.
33 R. C. Maurya, P. Patel and S. Rajput, *Synth. React. Inorg. Met.-Org. Chem.*, 2003, **33**, 801.
34 P. V. Rao, C. P. Rao, A. Sreedhara, E. K. Wegelius, K. Rissanen and E. Kolehmainen, *J. Chem. Soc., Dalton Trans.*, 2000, 1213.
35 P. A. Giesting and P. C. Burns, *Crystallogr. Rev.*, 2006, **12**, 205.
36 A. E. Vaughn, D. B. Bassil, L. B. Charles, S. A. Tucker and P. B. Duval, *J. Am. Chem. Soc.*, 2006, **128**, 10656.
37 D. M. Rudkevich, J. D. Mercer-Chalmers, W. Verboom, R. Ungaro, F. de Jong and D. N. Reinhoudt, *J. Am. Chem. Soc.*, 1995, **117**, 6124.
38 K. Takao and Y. Ikeda, *Inorg. Chem.*, 2007, **46**, 1550.
39 H. Sopo, J. Sviili, A. Valkonen and R. Sillanpaa, *Polyhedron*, 2006, **25**, 1223.
40 C. H. Weng, S. C. Cheng, H. M. Wei, H. H. Wei and C. J. Lee, *Inorg. Chim. Acta*, 2006, **359**, 2029.
41 P. Thuery, *Polyhedron*, 2007, **26**, 101.
42 B. Masci and P. Thuery, *Polyhedron*, 2006, **24**, 229.
43 M. T. Weller, M. E. Light and T. Gelbrich, *Acta Crystallogr., Sect. B: Struct. Sci.*, 2000, **56**, 577.
44 A. K. Sah, C. P. Rao, P. K. Saarenketo, E. K. Wegelius, E. Kolehmainen and K. Rissanen, *Eur. J. Inorg. Chem.*, 2001, 2773.
45 http://www.ccdc.cam.ac.uk/products/mercury/.
46 G. Bandoli, D. A. Clemente, U. Croatto, M. Vidali and P. A. Vigato, *J. Chem. Soc. D*, 1971, 1330.
47 A. F. Marinovich, R. S. O'Mahony, J. M. Waters and T. N. M. Waters, *Croat. Chim. Acta*, 1999, **72**, 685.
48 A. Gelasco and V. L. Pecoraro, *J. Am. Chem. Soc.*, 1993, **115**, 7928.
49 L. Salmon, P. Thuery and M. Ephritikhine, *Dalton Trans.*, 2004, 1635.
50 J. M. Sayer and P. Conlon, *J. Am. Chem. Soc.*, 1980, **102**, 3592.
51 R. H. Kayser and R. M. Pollack, *J. Am. Chem. Soc.*, 1977, **99**, 3379.
52 J. Suh and D. W. Min, *J. Org. Chem.*, 1991, **56**, 5710.
53 A. C. Dash and R. K. Nanda, *J. Am. Chem. Soc.*, 1969, **91**, 6944.
54 A. M. Herrera, G. N. Kalayda, J. S. Disch, J. P. Wilkstrom, I. V. Korendovych, R. J. Staples, C. F. Campama, A. Y. Zazarekno, T. E. Hass and E. V. Rybak-Akimova, *Dalton Trans.*, 2003, 4482.
55 D. K. Cabbiness and D. W. Margerum, *J. Am. Chem. Soc.*, 1970, **92**, 2151.
56 D. J. Evans, P. C. Junk and M. K. Smith, *Polyhedron*, 2002, **21**, 2421.