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Uranyl(VI) complexes with a diaminobisphenol from eugenol and *N*-(2-aminoethyl)morpholine: Syntheses, structures and extraction studies

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ABSTRACT

The syntheses and structural studies of an [O,N,O,N′]-type phenolic ligand [(*N*′,*N*′-bis(2-hydroxy-3-methoxy-5-(propen-2-yl)benzyl)-N-(2-aminoethyl)morpholine), (H_2L) and two new uranyl complexes of this ligand are described. The reaction between uranyl nitrate hexahydrate and H_2L in a 1:2 M ratio (M to H_2L) results in a uranyl complex of the formula $[UO_2(HL)(NO_3)(H_2O)]$ (**1**). In the presence of a base (triethylamine), with the same molar ratio, the uranyl complex $[UO_2(HL)_2]\cdot 2CH_3CN$ (**2**) is formed. The molecular structures H_2L, **1** and **2** were verified by X-ray crystallography. Both uranyl complexes are zwitterions with a neutral net charge. A comprehensive NMR-structural analyses of all compounds were performed in $CDCl_3$, DMSO-d_6 and pyridine-d_5. Complex **2** dissociates in all the studied NMR-solvents, forming a 1:1 complex and free ligand, but according to the spectra the formed complexes are not alike. The results of the ability of the ligand to extract the uranyl ion from water into dichloromethane are also presented.

1. Introduction

Although actinide elements are primarily associated with energy production or war technology, modern applications of these elements exist also in civil areas and medicine. Despite their wide use, our knowledge about the coordination chemistry of these metal ions is fairly limited, compared, for instance, to d-transition metal ions [1]. The uranyl ion ($[UO_2]^{2+}$) is found to be the most stable species of uranium in aqueous solutions *in vivo* [2]. The unique linear structure of the uranyl cation with an overall +2 charge prevents the use of effective chelating ligands that target spherical ions in three dimensions (e.g. EDTA, DTPA, etc.) [3]. It was noted recently that "no effective chelating agent is available for uranium, which should be considered a matter for some concern" [4]. So, finding an effective ligand to bind uranyl ions has a practical goal: the extraction of uranium from various media, even selectively [5–7]. For example Raymond et al. have made a series of extraction studies with carboxylate type ligands [8]. Recently the uranyl ion was encapsulated in order to improve its extraction [9]. Many good uranyl extractors contain a phenolate oxygen, which is a typical hard Lewis base and has a good affinity towards the hard uranyl ion [10]. Earlier [11] we have studied uranyl complexes with [O,N,O,N′]-type ligands, and the ability of these ligands to extract uranyl ions from water into dichloromethane. Our approach to this subject includes flexible bisphenolate ligands with nitrogen donors, as these ligands are capable of coordinating to uranyl ions by forming neutral complexes. One of the aims of this work is to prepare new phenolic ligands which are usable in biological systems. Eugenol ($C_{10}H_{12}O_2$) is an allyl chain-substituted guaiacol, i.e. 2-methoxy-4-(2-propenyl)phenol. This biological compound has several uses in health care and cosmetics [12]. A new ligand, H_2L (Scheme 1), was prepared from eugenol, formaldehyde and N-(2-aminoethyl)morpholine, and its coordination and extraction potential with uranyl ions were studied. *N*-(2-aminoethyl)morpholine brings to the ligand two nitrogen atoms as possible donors. In this work we report the preparation of the ligand H_2L and two of its uranyl complexes. The compounds are characterized by elemental analysis, NMR-spectroscopy and X-ray diffraction. Uranyl ion extractions tests were also performed.

2. Experimental

2.1. General information

N-(2-aminoethyl)morpholine (Aldrich), eugenol (Aldrich), triethylamine (Riedel), 37% formaldehyde (Riedel) and uranyl nitrate hexahydrate (Merck) were used as supplied. The ligand H_2L was synthesized by mainly following the procedure described by Burke et al. [13,14]. Details of the syntheses are described below.

Liquid-state ^1H, ^{13}C and 2 D PFG ^1H–^{13}C HMQC and HMBC NMR spectra were recorded in $CDCl_3$ at 30 °C with a Bruker Avance DRX 500 spectrometer equipped with a 5 mm diameter broad band inverse detection probe head operating at 500.13 MHz in ^1H, and 125.77 MHz in ^{13}C experiments. Spectra in pyridine-d_5 were recorded with a Bruker AVANCE DPX 250 FT NMR spectrometer.

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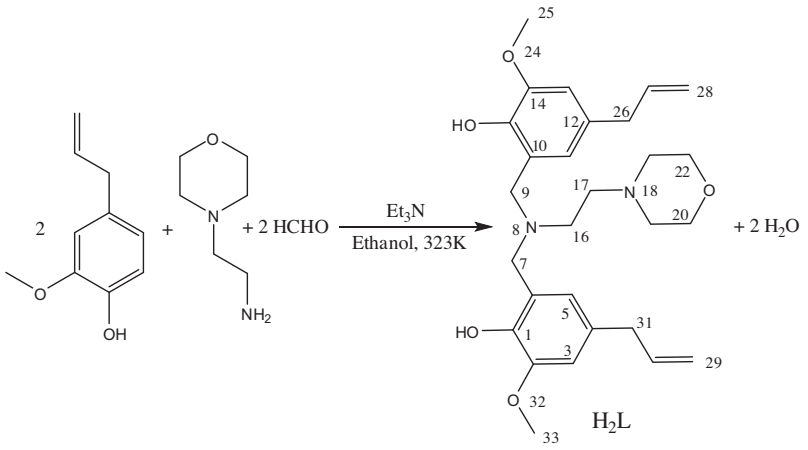


Scheme 1. The synthesis route to H_2L and the numbering system used.

^{1}H and ^{13}C NMR spectra were recorded either in $CDCl_3$, DMSO-d_6 or in pyridine-d_5 at 30 °C and chemical shifts are reported in ppm relative to $CDCl_3$ (δ 7.26, ^{1}H NMR), DMSO-d_6 (δ 2.50, ^{1}H NMR; 39.51, ^{13}C NMR) or pyridine-d_5 (δ 8.74, ^{1}H NMR; 150.35, ^{13}C NMR).

The solid-state NMR measurements were recorded with a Bruker Avance 400 spectrometer using 4.0 mm (50 μl) HRMAS-rotors at a 10 kHz spinning rate. The contact times for CP/MAS experiments for ^{13}C and ^{15}N were 2 and 3 ms, and the relaxation delays 4 and 5 s, respectively. For the non-quaternary suppression (NQS) experiments, the dephasing delay was set to 50 μs and for the short CP experiments, the contact time was set to 50 μs. Spinal-64 heteronuclear decoupling was used in all solid-state NMR experiments. The ^{13}C and ^{15}N chemical shifts were calibrated using carbonyl (at 176.03 ppm) and amine (at −347.4 ppm) resonances of glycine as an external standard.

Mass spectrometric measurements were performed using a Micromass LCT time of flight (TOF) mass spectrometer with electrospray ionization (ESI-MS). Elemental analyses were done using a VarioE1 III elemental analyzer. Single crystal X-ray measurements were performed using an Enraf Nonius Kappa CCD diffractometer. The uranyl extraction samples were analyzed with inductively coupled plasma optical emission spectrometry (ICP-OES) at 385.958 nm using a Perkin–Elmer Optima 4300DV instrument.

2.2. Ligand synthesis

Ligand H_2L was prepared by dissolving eugenol (2.46 mL, 16 mmol) in ethanol (20 mL) in a round bottom flask. N-(2-aminoethyl)morpholine (1.04 mL, 8.0 mmol), 36% formaldehyde water solution (6.0 mL, 79 mmol) and triethylamine (2.16 mL, 16.0 mmol) were added to the reaction mixture (Scheme 1). The reaction flask was placed in a water bath (50 °C) and the progress of the reaction was followed by HPLC. After 24 h, the solvent was evaporated in a rotary evaporator and the remaining brown syrup was dissolved in a small amount of ethanol (precipitation occurs in a hexane–acetone 3:2 mixture, but the resulting crude product requires further purification). The product was purified by silica gel chromatography (silica 60, hexane–acetone 3:2 v/v), recrystallized from ethanol four times and air dried. Yield 0.88 g (23%).

Elemental *Anal*: Calc. for $C_{28}H_{38}N_2O_5$: C, 69.7; H, 7.9; N, 5.8. Found: C, 69.8; H, 7.3; N, 5.5%.

^{1}H NMR (500 MHz, $CDCl_3$): 2.35 (t, 4H, morpholine ring –CH_2–N–CH_2–), 2.54 (t, 2H, N–CH_2–CH_2–N(8)), 2.61 (t, 2H, N–CH_2–CH_2–N(8)), 3.25 (d, 4H, Ar-CH_2–CH=), 3.66 (s, 4H, Ar-CH_2–N–CH_2–Ar), 3.70 (t, 4H, –CH_2–O–CH_2–), 3.80 (s, 6H, Ar-O–CH_3), 5.03 (m, 4H, CH=CH_2), 5.90 (m, 2H, CH=CH_2), 6.50 (s, 2H, ArC5–*H*), 6.59 (s, 2H, ArC3–*H*).

^{1}H NMR (250 MHz, pyridine-d_5): 2.31 (t, 4H, morpholine ring –CH_2–N–CH_2–), 2.55 (t, 2H, N–CH_2–CH_2–N), 2.78 (t, 2H, N–CH_2–CH_2–N), 3.38 (d, 4H, Ar-CH_2–CH=), 3.78 (t, 4H, –CH_2–O–CH_2–), 3.78 (s, 6H, Ar-O–CH_3), 3.96 (s, 4H, Ar-CH_2–N–CH_2–Ar), 5.12 (m, 4H, –CH=CH_2), 6.09 (m, 2H, –CH=CH_2), 6.86 (s, 4H, aryl *H*).

^{1}H NMR (500 MHz, DMSO-d_6): 2.23 (t, 4H, morpholine ring –CH_2–N–CH_2), 2.48 (t, 4H, N–CH_2–CH_2–N), 3.23 (d, 4H, Ar-CH_2–CH=), 3.55 (t, 4H, –CH_2–O–CH_2–), 3.57 (s, 4H, Ar-CH_2–N–CH_2-Ar), 3.74 (s, 6H, Ar-O–CH_3), 5.02 (m, 4H, –CH=CH_2), 5.92 (m, 2H, –CH=CH_2), 6.52 (s, 2H, ArC5–*H*), 6.66 (s, 2H, ArC3–*H*).

^{13}C NMR (126 MHz, $CDCl_3$): 39.53 (Ar-CH_2–CH=), 48.77 (N–CH2–CH_2–N(8)), 53.45 (morpholine ring –CH_2–N–CH_2–), 53.45 (Ar-CH_2–N–CH_2–Ar), 55.52 (N–CH_2–CH_2–N(8)), 55.73 (Ar-O–CH_3), 66.30 (–CH_2–O–CH_2–), 111.3 (ArC3), 115.2 (–CH=CH_2), 121.9 (ArC5), 122.5 (ArC6), 130.2 (ArC4), 137.6 (–CH=CH_2), 143.9 (ArC1), 147.3 (ArC2).

^{13}C NMR (63 MHz, pyridine-d_5): 40.54 (Ar-CH_2–CH=), 49.96 (N–CH_2–CH_2–N(8)), 54.37 (morpholine ring –CH_2–N–CH_2–), 55.25 (Ar-CH_2–N–CH_2-Ar), 56.18 (N–CH_2–CH_2–N(8)), 56.57 (Ar-O–CH_3), 67.30 (–CH_2–O–CH_2–), 113.1 (ArC3), 115.8 (–CH=CH_2), 124.3 (ArC5), 125.0 (ArC6), 130.8 (ArC4), 139.2 (–CH=CH_2), 146.4 (ArC1), 149.1 (ArC2).

^{13}C NMR (126 MHz, DMSO-d_6): 39.16 (Ar-CH_2–CH=), 48.52 (N–CH_2–CH_2–N(8)), 53.02 (morpholine ring –CH_2–N–CH_2–), 53.25 (Ar-CH_2–N–CH_2–Ar), 54.61 (N–CH_2–CH_2–N(8)), 55.69 (Ar-O–CH_3), 65.78 (–CH_2–O–CH_2–), 111.7 (ArC3), 115.2 (–CH=CH_2), 121.7 (ArC5), 123.4 (ArC6), 129.4 (ArC4), 138.0 (–CH=CH_2), 144.0 (ArC1), 147.4 (ArC2).

^{13}C NMR (126 MHz, CP/MAS): 40.33 (Ar-CH_2–CH=), 46.14 (N–CH2–CH_2–N(8)), 51.00–54.00 (morpholine ring –CH_2–N–CH_2– and Ar-CH_2–N–CH_2-Ar), 53.39, 56.05 (Ar-O–CH_3), 65.78 (–CH_2–O–CH_2–), 58.47 (N–CH_2–CH_2–N(8)), 108.9, 111.9 (ArC3), 113.7, 115.9 (–CH=CH_2), 120.8, 124.9 (ArC5), 123.2 (ArC6), 129.2 (ArC4), 137.7, 139.9 (–CH=CH_2), 145.5, 146.3 (ArC1), 148.8 (ArC2).

ESI-MS *m/z*: 483.29 $[H_2L+H]^+$.

2.3. Syntheses of the uranyl complexes

2.3.1. $[UO_2(HL)(NO_3)(H_2O)]$ (*1*)

$UO_2(NO_3)_2{\cdot}6H_2O$ (0.050 g, 0.10 mmol) and H_2L (0.10 g, 0.21 mmol) were dissolved separately in 1 mL CH_3CN. The solutions were combined and an immediate colour change from yellow

to red was observed. The reaction tube was kept at room temperature for two days and at 5 °C for another two days. The resulting dark red crystals of **1** were filtered off, washed once with diethyl ether (5 mL) and then air dried. Yield 0.077 g (77%).

Elemental *Anal.* Calc. for $C_{28}H_{39}N_3O_{11}U$: C, 40.4; H, 4.7; N, 5.1; Found: C, 40.5; H, 4.6; N, 5.0%.

^{1}H NMR (250 MHz, pyridine-d_5), (coordinated ligand): 1.95 (t, 4H, morpholine ring –C*H*$_2$–N–C*H*$_2$–), 2.49 (t, 2H, N–C*H*$_2$–CH$_2$–N(8)), 3.51 (d, 4H, Ar-C*H*$_2$–CH=), 3.61 (t, 2H, N–CH$_2$–C*H*$_2$–N(8)), 3.63 (s, 6H, –O–C*H*$_3$), 3.68 (t, 4H, –C*H*$_2$–O–C*H*$_2$–), 4.36, 5.61 (d, 4H, Ar-C*H*$_2$–N–C*H*$_2$-Ar), 5.15 (m, 4H, –CH=C*H*$_2$), 6.10 (m, 2H, –C*H*=CH$_2$), 6.93 (s, 2H, Ar*H*5), 7.01 (s, 2H, Ar*H*3).

^{1}H NMR (500 MHz, DMSO-d_6), (coordinated ligand): 2.01 (t, 4H, morpholine ring –C*H*$_2$–N–C*H*$_2$–), 2.55 (t, 2H, N–C*H*$_2$–CH$_2$–N(8)), 3.01 (t, 2H, N–CH$_2$–C*H*$_2$–N(8)), 3.27 (t, 4H, –C*H*$_2$–O–C*H*$_2$–), 3.37 (d, 4H, Ar-C*H*$_2$–CH=), 3.89 (s, 6H, Ar-O–C*H*$_3$), 5.03 (m, 4H, –CH=C*H*$_2$), 5.96 (m, 2H, –C*H*=CH$_2$), 6.77 (s, 1H, Ar*H*5), 6.85 (s, 1H, Ar*H*3); (uncoordinated ligand): 2.22 (t, 4H, morpholine ring –C*H*$_2$–N–C*H*$_2$–), 3.25 (d, 4H, Ar-C*H*$_2$–CH=), 3.52 (t, 4H, –C*H*$_2$–O–C*H*$_2$–), 3.76 (s, 6H, Ar-O–C*H*$_3$), 5.02 (m, 4H, –CH=C*H*$_2$), 5.92 (m, 2H, –C*H*=CH$_2$), 6.58 (s, 1H, Ar*H*5), 6.72 (s, 1H, Ar*H*3).

^{13}C NMR (63 MHz, pyridine-d_5), (coordinated ligand): 40.30 (Ar-*C*H$_2$–CH=), 51.80, 53.38 (N–*C*H$_2$–*C*H$_2$–N(8)), 53.95 (morpholine ring –*C*H$_2$–N–*C*H$_2$–), 56.17 (Ar-O–*C*H$_3$), 62.03 (Ar-*C*H$_2$–N–*C*H$_2$-Ar), 66.84 (–*C*H$_2$–O–*C*H$_2$–), 114.1 (Ar*C*3), 115.82 (–CH=*C*H$_2$), 122.3 (Ar*C*6), 129.4 (Ar*C*4), 139.6 (–CH$_2$–*C*H=CH$_2$), 152.9 (Ar*C*1), 160.1 (Ar*C*2).

^{13}C NMR (126 MHz, DMSO-d_6), (coordinated ligand): 46.10 (N–*C*H$_2$–CH$_2$–N(8)), 50.12 (N–CH$_2$–*C*H$_2$–N(8)), 53.74 (morpholine ring –*C*H$_2$–N–*C*H$_2$–), 55.80 (Ar-O–*C*H$_3$), 59.44 (Ar-*C*H$_2$–N–*C*H$_2$-Ar), 65.94 (–*C*H$_2$–O–*C*H$_2$–), 113.0 (Ar*C*3), 114.7 (–CH=*C*H$_2$), 122.1 (Ar*C*5), 125.8 (Ar*C*4), 139.0 (–*C*H=CH$_2$), 149.9 (Ar*C*2), 156.8 (Ar*C*1); (uncoordinated ligand): 48.54 (N(18)–CH$_2$–*C*H$_2$–N), 52.71 (morpholine ring –*C*H$_2$–N–*C*H$_2$–), 53.34 (Ar-*C*H$_2$–N–*C*H$_2$–Ar), 55.76 (Ar-O–*C*H$_3$), 65.57 (–*C*H$_2$–O–*C*H$_2$–), 112.1 (Ar*C*3), 115.4 (–CH=*C*H$_2$), 129.9 (Ar*C*4), 137.9 (–*C*H=CH$_2$), 143.8 (Ar*C*1), 147.4 (Ar*C*2).

Molecular ion species were not observed by ESI-MS.

2.3.2. $[UO_2(HL)_2]\cdot 2CH_3CN$ (**2**)

$UO_2(NO_3)_2\cdot 6H_2O$ (0.050 g, 0.10 mmol) and H_2L (0.10 g, 0.21 mmol) were dissolved separately in 1 mL CH_3CN. The solutions were combined and triethylamine (20 μL, 0.15 mmol) was added to the solution. An immediate colour change was observed and the red solution was kept at room temperature for two days and at 5 °C for another two days. The resulting orange crystals of **2** were filtered off, washed once with diethyl ether (5 mL) and then air dried. Yield 0.095 g (76%).

Elemental *Anal.* Calc. for $C_{56}H_{74}N_4O_{12}U$: C, 54.5; H, 6.0; N, 4.5. Found: C, 54.3; H, 6.1; N, 4.7%.

^{1}H NMR (500 MHz, $CDCl_3$), (dinuclear complex): 2.22 (m, 4H, morpholine ring –C*H*$_2$–N–C*H*$_2$–), 2.80, 2.89 (m, 2H, N–C*H*$_2$–C*H*$_2$–N), 3.51 (t, 4H, –C*H*$_2$–O–C*H*$_2$–), 3.52 (d, 2H, Ar-C(26)*H*$_2$–CH=), 3.57 (d, 2H, Ar-C(31)*H*$_2$–CH=), 4.04 (s, 3H, free Ar-O–C*H*$_3$), 4.38 (d, 1H, Ar-C(9)*H*$_2$–N–), 4.50 (d, 1H, Ar-C(7)*H*$_2$–N–), 5.03–5.20 (m, 4H, –CH=C*H*$_2$), 5.43 (s, 3H, coordinated Ar-O–C*H*$_3$), 5.49 (d, 1H, complex Ar-C(9)*H*$_2$–N–), 5.52 (d, 1H, complex Ar-C(7)*H*$_2$–N–), 6.05 (m, 2H, –C*H*=CH$_2$), 6.95 (s, 1H, ArC5–*H*), 7.02 (s, 1H, ArC3–*H*), 7.10 (s, 1H, ArC11–*H*), 7.42 (s, 1H, ArC13–*H*); (uncoordinated ligand): 2.38 (t, 4H, morpholine ring –C*H*$_2$–N–C*H*$_2$–), 2.58 (t, 2H, N–C*H*$_2$–CH$_2$–N(8)), 2.63 (t, 2H, N–CH$_2$–C*H*$_2$–N(8)), 3.27 (d, 4H, Ar–C*H*$_2$–CH=), 3.69 (s, 4H, Ar–C*H*$_2$–N–C*H*$_2$–Ar), 3.73 (t, 4H, –C*H*$_2$–O–C*H*$_2$–), 3.83 (s, 6H, Ar-O–C*H*$_3$), 5.03–5.20 (m, 4H, –CH=C*H*$_2$), 5.93 (m, 2H, –C*H*=CH$_2$), 6.51 (s, 2H, ArC5(/11)–*H*), 6.61 (s, 4H, ArC3(/13)–*H*).

^{1}H NMR (250 MHz, pyridine-d_5), (coordinated ligand): 2.24 (t, 4H, morpholine ring –C*H*$_2$–N–C*H*$_2$–), 2.91 (t, 2H, N–C*H*$_2$–C*H*$_2$–N), 3.44 (t, 4H, –C*H*$_2$–O–C*H*$_2$–), 3.56 (d, 4H, Ar-C*H*$_2$–CH=), 3.69 (s, 6H, Ar-O–C*H*$_3$), 3.76 (t, 2H, morpholine ring N–CH$_2$–C*H*$_2$–), 3.76 (t, 2H, N–C*H*$_2$–C*H*$_2$–N), 4.52, 5.41 (d, 4H, Ar-C*H*$_2$–N–C*H*$_2$-Ar), 5.13 (m, 4H, –CH=C*H*$_2$), 6.10 (m, 2H, –C*H*=CH$_2$), 7.06 (s, 1H, Ar*H*5), 7.11 (s, 1H, Ar*H*3); (uncoordinated ligand): 2.30 (t, 4H, morpholine ring –C*H*$_2$–N–C*H*$_2$–), 2.55 (t, 2H, morpholine ring N–C*H*$_2$–CH$_2$–), 2.78 (t, 2H, morpholine ring N–CH$_2$–C*H*$_2$–), 3.38 (d, 4H, Ar-C*H*$_2$–CH=), 3.76 (t, 4H, –C*H*$_2$–O–C*H*$_2$–), 3.78 (s, 6H, Ar-O–C*H*$_3$), 3.96 (s, 4H, Ar-C*H*$_2$–N–C*H*$_2$–Ar), 5.13 (m, 4H, –CH=C*H*$_2$), 6.10 (m, 2H, –C*H*=CH$_2$), 6.86 (s, 2H, Ar*H*5 and Ar*H*3).

^{1}H NMR (500 MHz, DMSO-d_6), (coordinated ligand): 2.00 (t, 4H, morpholine ring –C*H*$_2$–N–C*H*$_2$–), 2.54 (t, 2H, N–C*H*$_2$–CH$_2$–N(8)), 2.99 (t, 2H, N–CH$_2$–C*H*$_2$–N(8)), 3.27 (4H, –C*H*$_2$–O–C*H*$_2$–), 3.37 (d, 4H, Ar-C*H*$_2$–CH=), 3.90 (s, 6H, Ar-O–C*H*$_3$), 4.11, 4.66 (4H, Ar-C*H*$_2$–N–C*H*$_2$-Ar), 5.06 (m, 4H, –CH=C*H*$_2$), 5.97 (m, 2H, –C*H*=CH$_2$), 6.77 (s, 1H, Ar*H*5), 6.84 (s, 1H, Ar*H*3); (uncoordinated ligand): 2.23 (t, 4H, morpholine ring –C*H*$_2$–N–C*H*$_2$–), 2.48 (t, 4H, N–C*H*$_2$–C*H*$_2$–N), 3.23 (d, 4H, Ar-C*H*$_2$–CH=), 3.55 (t, 4H, –C*H*$_2$–O–C*H*$_2$–), 3.57 (s, 4H, Ar-C*H*$_2$–N–C*H*$_2$-Ar), 3.74 (s, 6H, Ar-O–C*H*$_3$), 5.02 (m, 4H, –CH=C*H*$_2$), 5.92 (m, 2H, –C*H*=CH$_2$), 6.52 (s, 1H, Ar*H*5), 6.66 (s, 1H, Ar*H*3).

^{13}C NMR (126 MHz, $CDCl_3$), (dinuclear complex): 39.47 (*C*26), 39.68 (*C*31), 46.58 (*C*16), 50.71 (*C*17), 54.16 (*C*19/*C*23), 55.81 (*C*33), 60.05 (*C*9), 61.47 (*C*7), 64.25 (*C*25), 66.88 (*C*20/*C*22), 112.4 (*C*3), 114.9 (*C*13), 115.2 (*C*29), 116.1 (*C*28), 121.9 (*C*5), 124.8 (*C*10), 126.1 (*C*6), 127.5 (*C*11), 129.8 (*C*4), 131.2 (*C*12), 137.4 (*C*30), 138.8 (*C*27), 150.3 (*C*2), 151.3 (*C*14), 152.9 (*C*15), 156.2(C1); (uncoordinated ligand): 39.72 (Ar-*C*H$_2$–CH=), 48.99 (N–CH$_2$–*C*H$_2$–N(8)), 53.67 (morpholine ring –*C*H$_2$–N–*C*H$_2$–), 55.15 (Ar-*C*H$_2$–N–*C*H$_2$-Ar), 55.74 (N–*C*H$_2$–CH$_2$–N(8)), 55.96 (Ar-O–*C*H$_3$), 66.54 (–*C*H$_2$–O–*C*H$_2$–), 111.5 (Ar*C*3), 115.4 (–CH=*C*H$_2$), 122.1 (Ar*C*5), 122.6 (Ar*C*6), 130.5 (Ar*C*4), 137.8 (–*C*H=CH$_2$), 144.1 (Ar*C*1), 147.5 (Ar*C*2).

^{13}C NMR (63 MHz, pyridine-d_5), (coordinated ligand): 40.52 (Ar-*C*H$_2$–CH=), 48.90 (N–CH$_2$–*C*H$_2$–N(8)), 52.00 (N–CH$_2$–*C*H$_2$–N(8)), 55.12 (morpholine ring –*C*H$_2$–N–*C*H$_2$–), 56.54 (Ar-O–*C*H$_3$), 60.91 (Ar-*C*H$_2$–N–*C*H$_2$-Ar), 67.48 (–*C*H$_2$–O–*C*H$_2$–), 114.3 (Ar*C*3), 115.4 (–CH=*C*H$_2$), 127.4 (Ar*C*6), 128.8 (Ar*C*4), 140.1 (–*C*H=CH$_2$), 151.4 (Ar*C*2), 158.3 (Ar*C*1); (uncoordinated ligand): 40.52 (Ar-*C*H$_2$–CH=), 49.96 (N–*C*H$_2$–CH$_2$–N(8)), 54.35 (morpholine ring –*C*H$_2$–N–*C*H$_2$–), 55.24 (Ar-CH$_2$–N–*C*H$_2$-Ar), 56.15 (N–*C*H$_2$–CH$_2$–N(8)), 56.54 (Ar-O–*C*H$_3$), 67.28 (–*C*H$_2$–O–*C*H$_2$–), 113.1 (Ar*C*3), 115.8 (–CH=*C*H$_2$), 125.0 (Ar*C*6), 130.7 (Ar*C*4), 139.2 (–*C*H=CH$_2$), 146.4 (Ar*C*1), 149.1 (Ar*C*2).

^{13}C NMR (126 MHz, DMSO-d_6), (coordinated ligand): 39.06 (Ar-*C*H$_2$–CH=), 46.04 (N–CH$_2$–*C*H$_2$–N(8)), 50.07 (N–*C*H$_2$–CH$_2$–N(8)), 53.76 (morpholine ring –*C*H$_2$–N–*C*H$_2$–), 55.76 (Ar-O–*C*H$_3$), 59.57 (Ar-*C*H$_2$–N–*C*H$_2$-Ar), 66.01 (–*C*H$_2$–O–*C*H$_2$–), 113.0 (Ar*C*3), 114.6 (–CH=*C*H$_2$), 122.2 (Ar*C*5), 125.8 (Ar*C*6), 125.9 (Ar*C*4), 139.1 (–*C*H=CH$_2$), 149.8 (Ar*C*2), 156.7 (Ar*C*1); (uncoordinated ligand): 39.06 (Ar-CH$_2$–CH=), 48.54 (N–CH$_2$–*C*H$_2$–N(8)), 53.03 (morpholine ring –*C*H$_2$–N–*C*H$_2$–), 53.27 (Ar-*C*H$_2$–N–*C*H$_2$-Ar), 54.61 (N–*C*H$_2$–CH$_2$–N(8)), 55.71 (Ar-O–*C*H$_3$), 65.79 (–*C*H$_2$–O–*C*H$_2$–), 111.7 (Ar*C*3), 115.2 (–CH=*C*H$_2$), 121.8 (Ar*C*5), 123.4 (Ar*C*6), 129.4 (Ar*C*4), 138.0 (–*C*H=CH$_2$), 144.0 (Ar*C*1), 147.4 (Ar*C*2).

^{13}C NMR (126 MHz, CP/MAS), (coordinated ligand + acetonitrile): 1.911 *C*H$_3$CN, 40.81 (Ar-*C*H$_2$–CH=), 50.85 (N–*C*H$_2$–*C*H$_2$–N), 53.37 (morpholine ring –*C*H$_2$–N–*C*H$_2$–), 54.84, 56.78 (Ar-O–*C*H$_3$), 61.83 (Ar–*C*H$_2$–N–*C*H$_2$–Ar), 66.14 (–*C*H$_2$–O–*C*H$_2$–), 113.0 (Ar*C*3), 113.7 (–CH=*C*H$_2$), 119.5, 121.7 (*C*H$_3$CN), 120.4 (Ar*C*5), 127.6 (Ar*C*6 and Ar*C*4), 139.4, 140.4 (–*C*H=CH$_2$), 153.1, 153.9 (Ar*C*2), 160.1 (Ar*C*1).

Molecular ion species were not observed by ESI-MS.

2.4. Uranyl extraction

A two phase extraction study was performed to determine the uranyl cation uptake from a water layer to a CH_2Cl_2 layer. To the bottom of a test tube was placed 3 mL of dichloromethane with the ligand diluted in it (0.10 g, 0.210 mmol). To the top of this layer was added 2 mL water with uranyl nitrate (c(U) = 6.25 mg/mL, n(U) = 0.0525 mmol). This led to a ratio of uranium to ligand of 1:4. For control purposes, a similar test tube was prepared without the ligand dissolved in the organic layer. The samples for ICP (V = 50 μl, diluted to 10 mL with water) were taken from the water layer over three days. One final sample was taken after three months from the beginning to find out the long term behaviour of the extraction process. The samples were analyzed with ICP-OES at 385.985 nm using a Perkin–Elmer Optima 4300DV instrument.

2.5. X-ray crystallography

Crystals suitable for single crystal X-ray measurements were obtained directly from the reaction tubes before filtration. This was necessary because the crystals of compound **2** readily decomposed by losing solvent molecules. The crystal data for compounds H_2L, **1** and **2**, along with other experimental details, are summarized in Table 1. The crystallographic data were collected at 123 K or 173 K on an Enraf Nonius Kappa CCD area detector diffractometer using graphite monochromatized Mo Kα radiation (λ = 0.71073 Å). Data collection was performed with φ and ω scans and the data were processed using DENZO-SMN v0.95.373 [15,16]. SADABS [17] absorption correction was applied to the data. The structures were solved by direct methods using the SHELXS-97 [18] or SIR-97 [19] programs and full matrix least squares refinements on F^2 were performed using the SHELXL-97 [20] program. The heavy atoms were refined anisotropically, except for the disordered carbon atoms in the side chains of the aromatic rings of **2**, which were refined isotropically. The CH hydrogen atoms were included at fixed distances using fixed displacement parameters from their host atoms while other H atoms were refined using fixed displacement parameters. Structure figures were drawn using ORTEP-3 for Windows [21].

Table 1
Summary of the crystallographic data for H_2L, **1** and **2**.

Compound	H_2L	**1**	**2**
Formula	$C_{28}H_{38}N_2O_5$	$C_{28}H_{39}N_3O_{11}U$	$C_{60}H_{80}N_6O_{12}U$
M_r	482.60	831.65	1315.33
Crystal system	monoclinic	monoclinic	triclinic
Space group (No.)	$C2/c$ (15)	$P2_1/c$ (14)	$P\bar{1}$ (2)
a (Å)	49.7208(9)	11.0770(2)	11.7999(2)
b (Å)	7.62060(10)	16.0070(3)	11.9321(3)
c (Å)	13.8123(2)	17.9394(3)	12.5360(3)
α (°)	90	90	68.009(2)
β (°)	92.8290(10)	100.4630(10)	82.047(2)
γ (°)	90	90	65.444(2)
V (Å^3)	5227.13(14)	3127.94(10)	1488.28 (7)
Z	8	4	1
Temperature (K)	123	173	173
D_{calc} (g cm^{-3})	1.226	1.766	1.468
μ (Mo Kα) (mm^{-1})	0.084	5.251	2.778
Collected reflections	10660	35248	21419
R_{int}	0.0289	0.057	0.056
Refined reflections	5709	6810	6473
Parameters	324	397	362
R_1[a]	0.0604 (0.0467)[b]	0.046 (0.031)	0.043 (0.041)
wR_2[c]	0.1081 (0.1012)	0.061 (0.057)	0.078 (0.077)
Largest difference in peak and hole (e Å^{-3})	0.221, −0.203	0.706, −0.806	1.009, −0.557

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] Values in parentheses for reflections with $I > 2.0\sigma(I)$.
[c] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ and $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP)]$, where $P = (2F_c^2 + F_o^2)/3$.

3. Results and discussion

3.1. Syntheses of the ligand and the uranyl complexes

The synthesis of the ligand is a simple condensation reaction, but due to the complexity of the reaction mechanism it is very sensitive to the reaction conditions. We have found several factors which directly affect the progress and yield of the reaction.

Most important among these is the solvent system used: wet polar solvents like alcohols are suitable for the reaction [11]. However this synthesis was performed in ethanol without added water because it gave the best yield, but this is an exception in the series of similar type syntheses [11,22–24]. Another important factor is that the reaction does not go to completion and after a certain reaction time it can even reverse direction. It seems that among the intermediates, the one with only one phenolic moiety attached to the amine is quite stable. The isolation process of the product was also difficult due to similar solubilities of eugenol, the reaction intermediates and the product. The mixture of hexane and acetone proved to give the best results in the efforts to precipitate the product from the reaction mixture. The same solvent mixture was used in further purification of H_2L with silica gel column chromatography.

Complex formation was studied in five different reactions by varying the stoichiometry of the reactants. The amounts of uranyl ions and solvent (acetonitrile) were kept constant, while the amounts of the ligand and the base (triethylamine) were varied (Table 2).

The possible reaction in tests 1 and 2 can be described by the Eq. (1):

$$[UO_2(NO_3)_2(H_2O)_x] + 2H_2L \rightarrow [UO_2HL(NO_3)(H_2O)](s) + H_3L^+ + NO_3^- + (x-1)H_2O \quad (1)$$

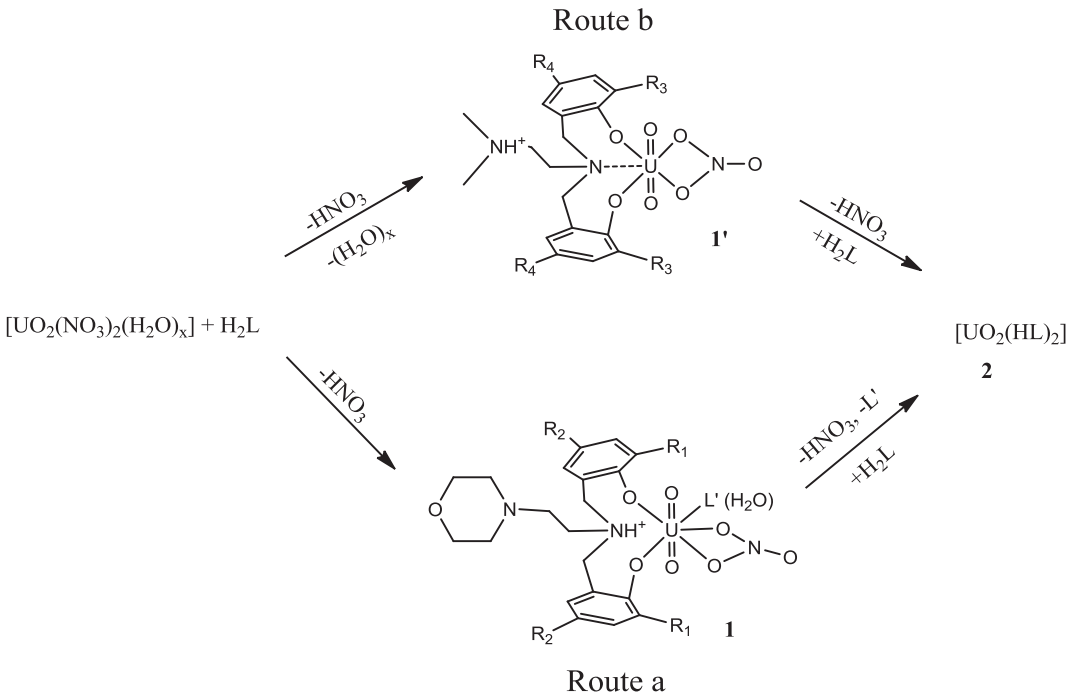
H_2L formed only mononuclear 1:1 complexes if no extra base was added to the reaction mixture. A complexation reaction occurred also in test 3 (notable colour change), but no crystals or solids were obtained. Under similar reaction conditions, it is possible to form a dinuclear complex, as was found earlier [22]. If this happened with H_2L, the complex must be diphenoxo-bridged.

If triethylamine is added to the reaction mixture, as was done in tests 4 and 5, an acetonitrile adduct of the 1:2 complex is formed, according to the reaction Eq. (2) (x is probably 4).

$$[UO_2(NO_3)_2(H_2O)_2]\cdot xH_2O + 2H_2L + 2Et_3N \rightarrow [UO_2(HL)_2]\cdot 2CH_3CN(s) + 2[Et_3NH]^+ + 2NO_3^- + (2+x)H_2O \quad (2)$$

Table 2
Summary of the performed reactions and the isolated uranyl complexes. The U:H_2L:B ratio refers to the ratio of uranyl ion, ligand and base (B = triethylamine).

Reaction	U:H_2L:B	Isolated complex
1	1:1:0	$[UO_2(HL)(NO_3)(H_2O)]$ (**1**)
2	1:2:0	$[UO_2(HL)(NO_3)(H_2O)]$ (**1**)
3	1:1:1	red solution
4	1:2:1	$[UO_2(HL)_2]\cdot 2CH_3CN$ (**2**)
5	1:2:2	$[UO_2(HL)_2]\cdot 2CH_3CN$ (**2**)



Scheme 2. Route (a) describes the formation of the uranyl complexes in this work. In H_2L (Route a) R_1 = OMe, R_2 = $CH_2CH{=}CH_2$. Route (b) is the one found in Ref. [11] using the H_2L ligand shown in 1′ with R_3 = R_4 = Me.

If the amount of water in the reaction mixture is reduced by using a drying agent, the reaction can lead to product 1′, presented in Scheme 2 (Route b). These reactions for Route b were found in the experiments made by Sopo et al. [11] using N,N-bis(2-hydroxy-3,5-dimethylbenzyl)-N′,N′-dimethylethylenediamine as a ligand, which has an [O,N,O,N′]-donor set similar to H_2L in this work. Several experiments were made to achieve a complex of type 1′ for H_2L, but they were not successful.

In complexes **1** and **2**, HL^- is in a zwitterionic form: the nitrogen (N8) is protonated while both phenolic oxygens bear a negative charge. The net charge in both complexes is zero. The colour of the reaction mixtures remained red in all cases after the isolation of the crystals formed, indicating that the crystallization was incomplete. Thus it is also possible that a 1:1 complex with a proton at N18 (route b) is formed as a minor component, but it stays in solution.

Complex **1** is quite soluble in polar solvents like alcohols and DMSO but its solubility is poor in slightly polar or non-polar solvents. Complex **2** is also quite soluble in slightly polar solvents like chloroform and dichloromethane. However both complexes (**1** and **2**) decompose on dissolving. This will be discussed in the NMR part of this chapter.

3.2. Structural studies of the ligand and its uranyl complexes

The molecular units of H_2L, **1** and **2** are presented in Figs. 1–3. Selected bond lengths and angles of **1** and **2** are presented in Table 3. The structure of H_2L is normal for a diaminobisphenol in which

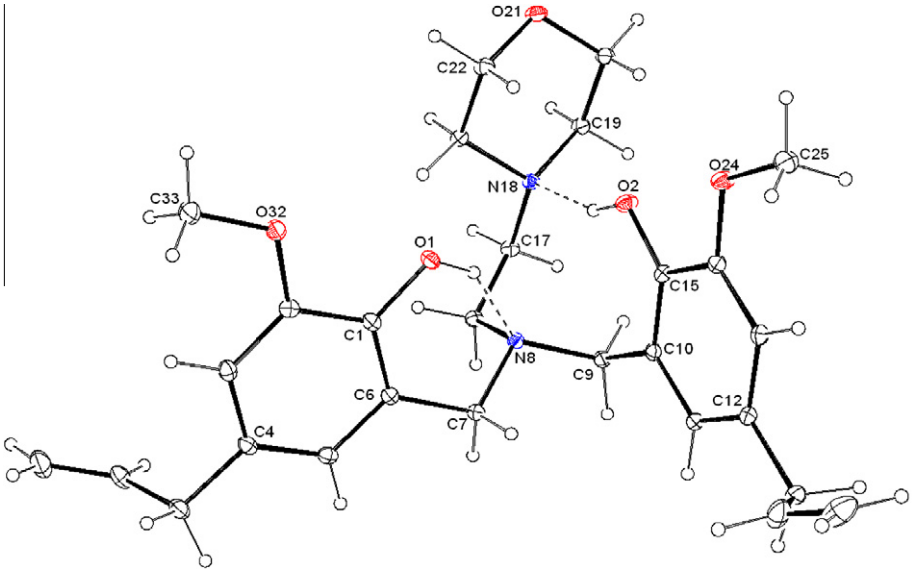


Fig. 1. The molecular structure of H_2L. The intramolecular H bonds between H(O1) and N8, and H(O2) and N18 are shown by dashed lines. Thermal ellipsoids have been drawn at the 20% probability level.

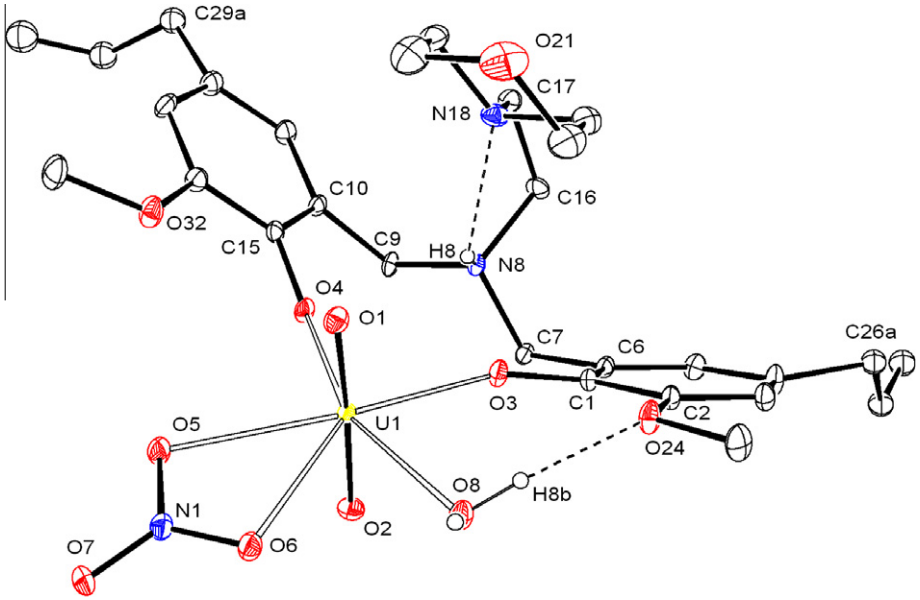


Fig. 2. The molecular structure of $[(UO_2(HL)(NO_3)(H_2O)]$ (**1**). Thermal ellipsoids have been drawn at the 20% probability level. The CH hydrogen atoms have been omitted for clarity. The $CH_2CH{=}CH_2$ groups at C4 and C14 are disordered over two positions in about a 1:1 ratio. Only the atoms in part a are shown.

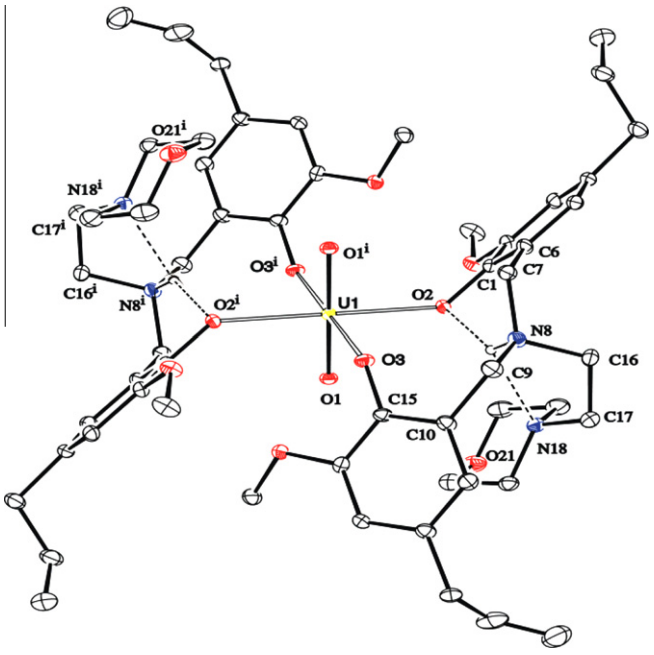


Fig. 3. The molecular structure of $[UO_2(HL)_2]\cdot 2CH_3CN$ (**2**). Thermal ellipsoids have been drawn at the 30% probability level. The CH hydrogen atoms and the acetonitrile molecules have been omitted for clarity. Symmetry operation: $2-x$, $1-y$, $-z$.

Table 3
Selected bond lengths (Å) and angles (°) for **1** and **2**.

Complex **1**		Complex **2**	
Bond lengths			
U(1)–O(1)	1.788(3)	U(1)–O(1)	1.795(2)
U(1)–O(2)	1.782(3)	U(1)–O(1)^{i}	1.795(2)[a]
U(1)–O(3)	2.196(3)	U(1)–O(2)	2.270(2)
U(1)–O(4)	2.179(2)	U(1)–O(3)	2.287(2)
U(1)–O(5)	2.545(3)		
U(1)–O(6)	2.533(3)		
U(1)–O(8)	2.488(3)		
C(1)–O(3)	1.337(4)	C(1)–O(2)	1.333(4)
C(15)–O(4)	1.335(4)	C(15)–O(3)	1.333(4)
Bond angles			
O(1)–U(1)–O(2)	174.12(13)	O(1)–U(1)–O(1)^{i}	180
O(1)–U(1)–O(3)	93.81(13)	O(1)–U(1)–O(2)	88.95(10)
O(1)–U(1)–O(4)	92.32(12)	O(1)–U(1)–O(2)^{i}	91.05(10)
O(2)–U(1)–O(3)	90.22(13)	O(1)–U(1)–O(3)	92.72(10)
O(2)–U(1)–O(4)	92.20(12)	O(1)–U(1)–O(3)^{i}	87.28(10)
O(3)–U(1)–O(4)	86.38(10)	O(2)–U(1)–O(3)	82.51(9)
O(3)–U(1)–O(8)	73.48(10)	O(2)–U(1)–O(3)^{i}	97.49(9)
O(4)–U(1)–O(5)	84.39(10)		
O(5)–U(1)–O(6)	50.38(9)		
O(6)–U(1)–O(8)	65.57(10)		
C(1)–O(3)–U(1)	161.5(3)	C(1)–O(2)–U(1)	137.2(2)
C(15)–O(4)–U(1)	159.6(3)	C(15)–O(3)–U(1)	140.4(2)
τ_1 versus τ_2[b]	47.2(2)		55.3(2)

[a] Generated by inversion.
[b] Dihedral angle between the planes of the phenyl rings: C1,..., C6 and C10,..., C15.

two intramolecular hydrogen bonds (O1–H1O···N8 and O2–H2O···N18) control the conformation of the ligand [22,25].

In **1** the coordination sphere around U is pentagonal bipyramidal and in **2** it is compressed octahedral. In both complexes the ligands behave in a zwitterionic manner with the protons at N(8). Only this nitrogen in the ligand is geometrically available for coordination, as in the 1:1 uranyl complex of N,N-bis(2-hydroxy-3,5-dimethylbenzyl)-N′,N′-dimethylethylenediamine [11], but now it is protonated and thus coordination is not possible. This feature is somewhat surprising because the charge balance could also be achieved by protonation of N(18) instead, which this would enable the coordination of N(8) to the uranyl ion. The U–O(phenolato) bonds in **1** are approximately 0.30 Å shorter than the U–O bonds to the coordinated nitrate ions and water molecules [26]. This can be understood because the O atoms in the nitrate ions and water molecules are weak donor atoms.

There is also a difference between the lengths of the U–O(phenolato) bonds of complexes **1** and **2**. These bonds are approximately 0.1 Å shorter in **1** compared to those in **2**. This indicates that the phenolato donors in **1** (a 1:1 complex) bond more strongly to the uranyl ion than in **2**. In a way this explains why the 1:2 complexes are not very stable in strongly coordinating solvents. This is

discussed in the section on NMR studies. The C–O–U bond angles are closer to linearity in **1** than in **2**; in **1** they are about 20° bigger than in **2**. The linearity of the C–O–U angles is another indication of stronger U–O(phenolato) bonds in **1**.

The morpholine moiety attached to the ligand does not form any bonds with the uranium atom. This is partly expected when one considers the Lewis basicity of the phenolate oxygens versus the nitrogen and oxygen atoms in the morpholine moiety. The linear structure of the uranyl ion also limits the coordination of the ligands to only the equatorial positions of the metal, and combining these facts there is hardly any available coordination space for the heteroatoms of the morpholine group.

In the solid state, the morpholine moiety is folded on top of the complex in **1** (Fig. 2), forming a cup-like structure. In **2**, two similar cup-like structures (Fig. 3) are also formed on both sides of the coordination sphere, resulting for the whole molecule a structure in which the uranyl ion is inside of a capsule. The main reason for these structural arrangements is the intramolecular N8–H8···N18 hydrogen bond. Another reason for this arrangement can be that in this way the oxygen and nitrogen atoms of the morpholine units are brought into a more polar environment. In compound **1**, one of the H atoms of the water molecule forms an intramolecular hydrogen bond to O24, and another to O1 in the neighbouring molecule, forming H-bonded dimeric units which pack together *via* weak van der Waals interactions (Fig. 4).

These observations give some evidence about the importance and strength of the internal hydrogen bonds in the conformation of the complex. Although the ligand is flexible enough to enable the coordination of N(8) to the uranyl ion, this would lead to a different conformation for the complex, as the hydrogen bonding between the nitrogens would be prevented and the morpholine moiety would most likely point away from the uranyl centre.

Structural comparisons between complexes **1** and **2** and two other complexes with a similar [O,N,O,N′]-donor set ligand (Sopo et al. [11]) reveal almost parallel structural properties between the complexes. Also two uranyl azacalixarene (*p*-methyl-N-benzyltetrahomodiazacalix[4]arene) compounds with an [O,N,O,O,N,O]-donor set ligand presented by Thuéry et al. [27,28] have structural similarities with the previous complexes.

If the complexation reaction of H_2L with the uranyl ion is carried out without an extra base, a 1:1 complex (U to L) (**1**) is crystallized out, in which the coordination sphere around the U(VI) ion is pentagonal bipyramidal. In two 1:1 uranyl calixarene complexes [27], only half of the possible four O donors are coordinated to the uranyl ion, and two nitrogens are protonated. The ligand is bonded "externally" to the uranyl ion and two nitrate ions fulfil the coordination sphere around the uranyl ion.

In the presence of an extra base, the ligand H_2L used in this work and the one mentioned in Ref. [11] form zwitterionic 1:2 (U to L) complexes with an octahedral coordination geometry around the uranyl ion. Also azacalixarene forms a similar complex in the presence of base [28]. Now all four phenolate oxygens of the calixarene ligand bond to the uranyl ion and both nitrogen donors of the ligand are protonated. Positively charged nitrogen atoms in close proximity to uranium seem not to hinder the formation of the complex, and the uranyl ion is placed inside the calixarene ring. On the other hand, in **2** the proton is not transferred to other nitrogen atom, which is further away from the uranyl ion, although this possibility is provided by the ligand.

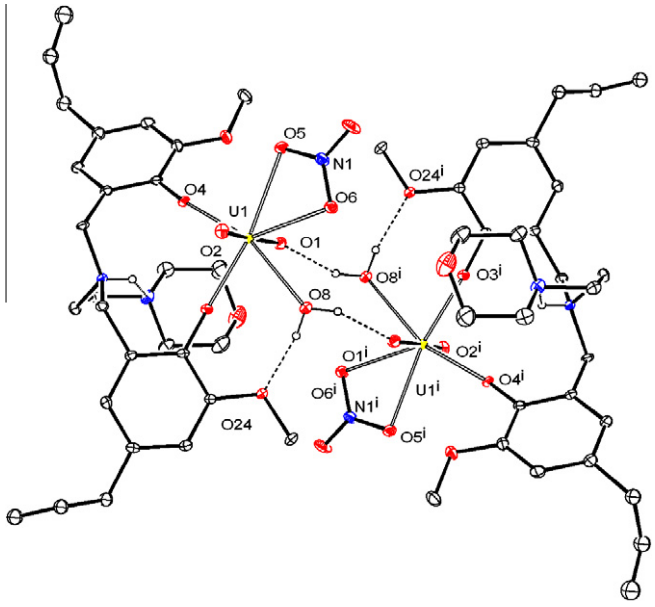


Fig. 4. The water molecules form hydrogen bond bridges in **1** generating a dimeric unit.

3.3. NMR studies

Compounds H_2L and **2** are very soluble in chloroform and this allows the measurement of their ^1H NMR spectra in $CDCl_3$, but as **1** had a low solubility in $CHCl_3$ the NMR spectra of all compounds (H_2L, **1** and **2**) were recorded in DMSO-d_6 and pyridine-d_5, in which all the substances readily dissolved. The NMR spectra of all the compounds in DMSO were analyzed with ^1H, ^{13}C, DEPT, HMQC and HMBC techniques in order to explain satisfactorily all the chemical shifts in the spectra. The proton and carbon spectra were also recorded in pyridine-d_5 to find out if there are signals under the solvent residual peaks of DMSO. The peak interpretation of the NMR spectra is described in Chapters 2.2.–2.3.

DMSO has good solvating properties with strong coordinating and H bonding properties. In the ^1H NMR spectra of H_2L in $CDCl_3$ and DMSO-d_6 there is a notable difference; in $CDCl_3$ it appears that the conformation with an intramolecular H bond (the one found in the solid state) remains in solution, but in DMSO-d_6 the intermolecular H bonds dominate, causing another conformation for H_2L.

For the complexes dissolved in DMSO, one can clearly see the partial dissociation of the ligand from the uranyl ion. For example, in the ^1H NMR spectra of **1** and **2** (in DMSO) the same peaks are seen that are found in the spectra of the free ligand H_2L, but also a similar battery of peaks that can be identified as the uranyl complex is present. In **1** the amount of free ligand is 30% and in **2** it is 50%. These spectral data suggest that both 1:1 and 1:2 complexes in DMSO decompose to a similar 1:1 complex.

On the contrary, in pyridine **1** is stable towards dissociation (only very small peaks of the ligand H_2L are seen in the spectra), but **2** dissociates totally to a 1:1 complex, as seen in DMSO. The 1:1 complexes in DMSO and pyridine are not identical although their spectra resemble each other. The reason for the small differences is the coordination of the solvent (DMSO or pyridine) as an extra ligand to the uranyl ion.

The chemical shifts of the coordinated ligand atoms compared to the ones of the free ligand depend on the electronic and conformational changes due to the complex formation. In the studied compounds, the shifts of the coordinated ligand atoms are generally not very different from those of the free ligand. However it was possible to assign their origins by comparing the spectra of the free and coordinating ligands using the spectral analysing methods mentioned above. In this work the way to follow the conformational changes of the ligand is to look at the signals of the prochiral hydrogens on carbon atoms 7 and 9.

In the ^1H spectra of **1** and **2** recorded in pyridine, the hydrogens at C7 and C9 give doublets in the lower field region, but these hydrogens give a singlet in the spectra of the pure ligand and

uncoordinated ligand. The ^{1}H NMR spectra of **1** and **2** recorded in DMSO produce such broad signals for the hydrogens at C7 and C9 that it is impossible to locate their exact positions.

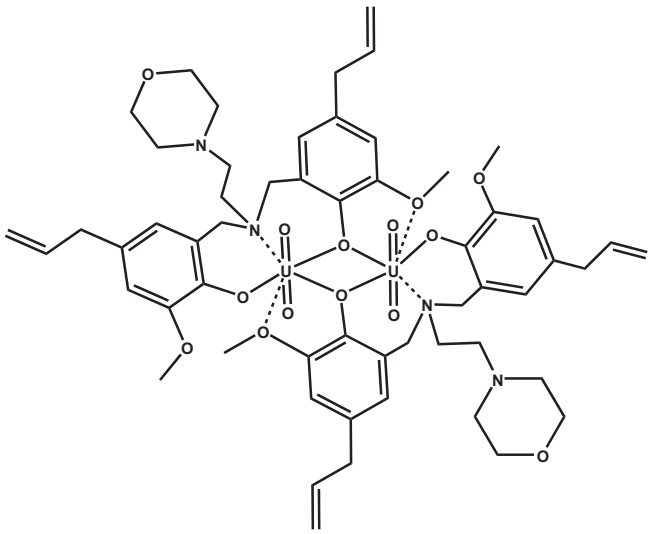
The ^{1}H NMR spectrum of **2** recorded in chloroform shows quite a different behaviour. The peak pattern, especially in the aromatic region of the spectrum, indicates that the complex is not stable in chloroform either, but since the solvent cannot offer a donor for coordination, a different 1:1 complex from that formed in pyridine or in DMSO is produced. One obvious possibility is that the complex is dinuclear with the formula $[(UO_2)_2(L)_2]$ (**3**). Hence one can find the signals for a free ligand and also the signals of the uranyl complex which are different from those of **2** in pyridine or in DMSO. The formation of this new complex can be explained according to reaction (3), in which the zwitterionic complex is broken forming complex **3** and a free ligand.

$$2[UO_2(HL)_2] \rightarrow [(UO_2)_2(L)_2] + 2H_2L \quad (3)$$

The ^{1}H NMR data strongly support the structure of $[(UO_2)_2(L)_2]$ described in Scheme 3. Especially, four different new aromatic signals and a signal for a coordinated ArOMe group at 5.43 ppm support the structure of **3**. The methoxy groups from one phenolic moiety can take the fifth coordination site around the uranyl ion in the *xy*-plane. This explains why a methyl singlet of the methoxy group at 5.43 ppm is at so low a field. More support for **3** can be obtained from the literature: the dimerization of the uranyl complex, UO_2(salophen)L (L = DMF, DMSO), occurs also in non-coordinating chloroform [29].

Several efforts to obtain crystals of this dinuclear complex were not successful. One reason for this failure can be seen from spectrum recorded in chloroform: it seems that the complex is decomposed in $CDCl_3$ by moisture. This is indirectly observed from the increase of the integrals related to the free ligand if the spectrum is measured as a function of time. The explanation for this phenomenon is most likely that moisture causes the decomposition and it also prevents the crystallization. If a chloroform solution of $[UO_2(HL)_2]$ (**2**) is evaporated to dryness and the residue (H_2L and **3**) is dissolved in acetonitrile, **2** is formed again.

Finally the coordination of the N8 nitrogen to the uranyl centre in deuterated solutions of complexes **2** and **3** forms another question of interest. The formation of the dinuclear complex **3** in chloroform most likely causes N8 to coordinate to the uranyl ion. If ^{1}H NMR data in $CHCl_3$ is compared to those in other solvents, one comes to the conclusion that also in pyridine this nitrogen is coordinated to the U atom. The pyridine solvent can accept a proton from the coordinated ligand. The observed low field doublets in the spectra, similar to those observed in chloroform, support this assumption. In DMSO, however, the situation remains somewhat uncertain: although broad signals from these hydrogens are observed in the spectra of **1** and **2**, they appear in a higher field region, and their broadness indicates conformational flexibility around N8 and thus the presence of a proton at N8.



Scheme 3. The suggested structure of the dinuclear complex **3** in chloroform, based on its NMR data.

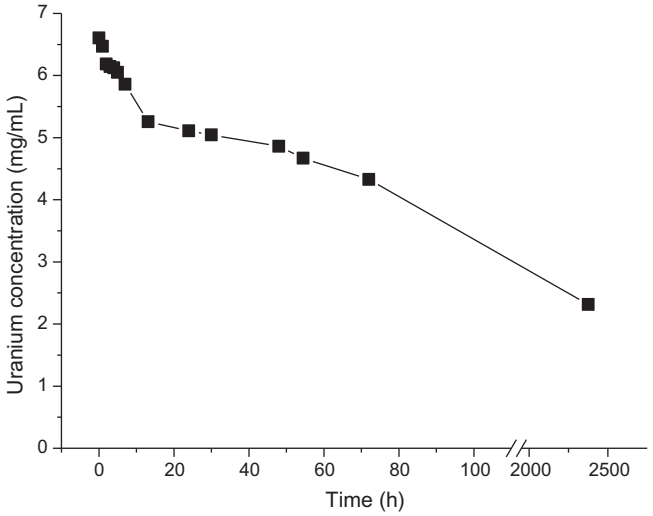


Fig. 5. The result of the uranyl extraction study.

Because almost all NMR spectra of the complexes recorded in solution indicated that the complexes dissociate, ^{13}C NMR CP/MAS spectra of H_2L and **2** were also recorded. However, the chemical shifts of the carbon atoms around N8 were quite similar and no confirmation of either proton transfer or nitrogen coordination in solution could be totally ensured.

3.4. Uranyl ion extraction studies

The result of the uranyl ion extraction study at room temperature (*ca.* 22 °C) is shown in Fig. 5. The experimental setup is described in Section 2.4. With this ligand, the transfer of the uranyl ion from the water layer to the CH_2Cl_2 layer was 34% in three days and 65% in three months. At the same time, the uranium concentration in the control sample was constant. The organic layer turned from colourless to red during the test time, indicating complex formation, but no crystals were obtained. The reason for the low extraction results of H_2L is found from NMR studies in chloroform; the 1:2 complex decomposes to the free ligand and the dinuclear uranyl complex, which is not very stable in moist dichloromethane. This causes the slow and inefficient extraction process.

4. Conclusion

In conclusion, we have found that $UO_2(NO_3)_2{\cdot}6H_2O$ reacts with the phenolic ligand *N'*,*N'*-bis(2-hydroxy-3-methoxy-5-(propen-2-yl)benzyl-*N*-(2-aminoethyl)morpholine, H_2L, in CH_3CN to form two different dioxouranium(VI) complexes. The complex of the formula $[UO_2(HL)_2]{\cdot}2CH_3CN$ was obtained from acetonitrile when triethylamine was added to the reaction solution; without triethylamine the formed uranyl complex had the formula $[UO_2(HL)(NO_3)(H_2O)]$. Both formed complexes have a zwitterionic nature in the solid state with bideprotonated phenol groups, but the

complexes are formally electrically neutral as their charge is balanced by a protonated quaternary nitrogen atom in the ligand. The behaviour of the complexes in organic solvents was surprising. In pyridine **1** keeps its 1:1 nature, but in DMSO **1** dissociates partly (30%) to the free ligand and a 1:1 complex. Complex **2** dissociates to the free ligand and 1:1 complexes in pyridine, DMSO and chloroform. However in chloroform the 1:1 complex is dinuclear and is sensitive to water.

The capability of the ligand to extract uranium from a water layer to an organic layer was examined and it was found that 34% of uranium was transferred within three days and 65% within three months. It is a weaker extractor compared to aminoalcohol bisphenols [23] and alkyl bisphenols [24].

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Appendix A. Supplementary data

CCDC 782116, 782116 and 782118 contains the supplementary crystallographic data for H_2L, **1** and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223–336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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