



Uranyl(VI) binding by bis(2-hydroxyaryl)diimine and bis(2-hydroxyaryl)diamine ligand derivatives. Synthetic, X-ray, DFT and solvent extraction studies



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ABSTRACT

The interaction of uranyl(VI) nitrate with a series of bis(2-hydroxyaryl)imine (H_2L^1 – H_2L^5) and bis(2-hydroxyaryl)amine (H_2L^8 , H_2L^9) derivatives incorporating 1,3-dimethylenebenzene or 1,3-dimethylene-cyclohexane bridges between nitrogen sites is reported. Crystalline complexes of type $[UO_2(H_2L)(NO_3)_2]$ (where H_2L is H_2L^1 – H_2L^4) were isolated from methanol. X-ray structures of the complexes of H_2L^1 , H_2L^2 and H_2L^4 show that each of these neutral ligands bind to their respective UO_2^{2+} centres in a bidentate fashion in which coordination only occurs via each ligand's hydroxy functions. Two bidentate nitrate anions complete the metal's coordination sphere in each complex to yield hexagonal bipyramidal coordination geometries. A density functional theory (DFT) investigation of $[UO_2(H_2L^1)(NO_3)_2]$ in a simulated methanol environment is in accord with this complex maintaining its solid state conformation in solution. Solvent extraction experiments (water/chloroform) employing H_2L^1 – H_2L^7 in the organic phase and uranyl(VI) nitrate in the aqueous phase showed that both amine derivatives, H_2L^8 and H_2L^9 , yielded enhanced extraction of UO_2^{2+} over the corresponding imine derivatives, H_2L^1 and H_2L^2 . These results were further compared with those obtained for the corresponding Schiff bases incorporating 1,2-phenylene and 1,2-cyclohexane bridged ligands, H_2L^6 and H_2L^7 ; these more rigid systems also yielded enhanced extraction of UO_2^{2+} relative to the more flexible Schiff bases H_2L^1 – H_2L^5 . A very significant synergistic enhancement of the extraction of UO_2^{2+} by H_2L^1 – H_2L^4 and H_2L^7 was observed in the presence of a 10-fold excess of *n*-octanoic acid; the influence of pH on extraction efficiency was also investigated. A parallel set of experiments employing H_2L^1 – H_2L^9 as extractants for europium(III) nitrate indicated a clear uptake preference for UO_2^{2+} over Eu^{3+} in all cases; separation of the uranyl ion from the rare earths is an important objective in mineral processing.

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1. Introduction

The coordination chemistry of uranyl(VI) has received increasing attention over recent years [1,2]. Many such studies [3–6] were motivated by the awareness that an enhanced understanding of the complexation behaviour of this ion has implications for the winning, processing and use of uranium as well as for the appropriate control, processing and storage of nuclear wastes

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[7–16]. As a consequence, a number of studies have focused on ligand design for selective uranium uptake [17–20], with particular studies focused on the separation of actinides from the lanthanides [21–25] – metals which occur together in nature and nuclear wastes. However, in general, such separations are inherently challenging due to the generally similar chemistry of these ions.

In the above context it is noted that a number of Schiff base ligands have been employed for uranyl extraction [23,26,27]. For example, H_2L^6 (salophen), has been shown to form robust neutral 1:1 uranyl chelate complexes of composition $[UO_2(L^6)S]$, each incorporating a solvent molecule ($S = DMF, DMSO, H_2O$) [28,29]. Ligand species of this type incorporating a short spacer group

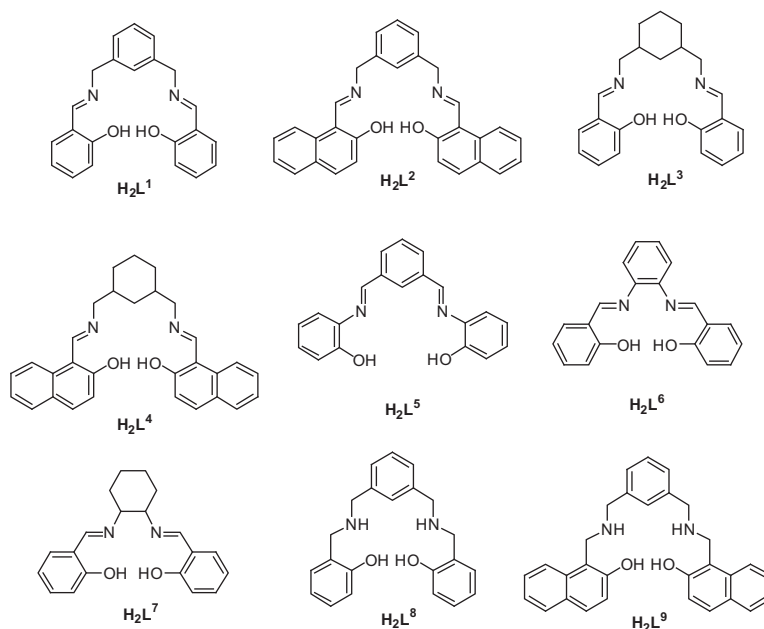
(in the above case a 1,2-phenylene group) as well as structure-related species have been shown to be extracted with high efficiency into an organic phase [30]. However, bis(2-hydroxyaryl)imines, where the two terminal chelating domains are linked by extended spacer groups, have received considerably less attention even though individual examples of the latter ligands have been known for a considerable time [31].

We now report synthetic, X-ray, computational and solvent extraction studies involving the interaction of uranyl(VI) nitrate with the bis(2-hydroxyaryl)diimine derivatives (H_2L^1 – H_2L^5) and bis(2-hydroxyaryl)diamine derivatives (H_2L^8 and H_2L^9), incorporating 1,3-dimethylenebenzene or 1,3-dimethylenecyclohexane units as linking backbones. The results are compared with those for the related Schiff base (H_2L^6 , H_2L^7) ligand derivatives. Comparative results for the extraction of europium(III) with H_2L^1 – H_2L^9 are also presented.

and (H_2L^7) (from (\pm)-*trans*-1,2-diaminocyclohexane and salicylaldehyde) [36,37] were carried out by the respective literature procedures.

2.2. General procedure for the synthesis of Schiff base ligands H_2L^2 – H_2L^4

A methanol solution of the required diamine and aldehyde in a 1:2 M ratio was heated under reflux for ~ 4 h, on cooling, to yield a yellow solid in each case which was removed by filtration. Crude H_2L^3 was dissolved in $CHCl_3$, washed with distilled water, and the organic solvent was dried with anhydrous $MgSO_4$ and subsequently removed to obtain the pure compound. All products were washed with cold methanol, and dried under vacuum. Characterisation details are given below.



2. Experimental

2.1. Materials and instrumentation

All reagent and solvents were obtained from commercial sources and used without further purification. The 1H and ^{13}C NMR spectra were recorded on a Bruker Avance DRX-500 spectrometer with $DMSO-d_6$ and $CDCl_3$ as solvents. Mass spectrometry (ESI-MS) analyses were carried out using a Bruker ESQUIRE mass spectrometer. Infrared spectra were recorded on a BioRad Excalibur FTS 3000-Spectrometer using KBr pellets. Elemental analysis (C, H, and N) were carried out on a Carlo Erba (EA 1108) Analyser. UV data were collected using a Perkin Elmer type Lambda 25 spectrophotometer in the range 200–1200 nm. The syntheses of H_2L^1 (from *m*-xylylenediamine and salicylaldehyde) [32,33], H_2L^5 (from *o*-aminophenol and isophthalaldehyde) [34], H_2L^6 (from 1,2-phenylenediamine and salicylaldehyde) [33,35]

2.3. Characterisation of Schiff base ligands H_2L^1 – H_2L^4

2.3.1. α,α' -Bis(salicylimino)-*m*-xylene (H_2L^1)

From *m*-xylylenediamine and salicylaldehyde. Yield = 74%, 1H NMR (500 MHz, $DMSO-d_6$, 25 °C, TMS): δ = 13.42 (s, 2H, OH \cdots N), 8.72 (s, 2H, CH=N), 7.48 (dd, J = 8.6, 8.7 Hz, 2H, C_6H_4), 7.38 (t, J = 7.7, 7.5 Hz, 1H, C_6H_4), 7.35 (s, 1H, C_6H_4), 7.33 and 6.91 (t, J = 11.9, 8.2, 7.5 Hz, 4H, C_6H_4O), 7.27 (d, J = 7.6 Hz, 2H, C_6H_4O), 6.87 (d, J = 8.2 Hz, 2H, C_6H_4O), 4.82 (s, 4H, CH_2). ESI-MS (MeOH): m/z 345 [$M+H^+$]. IR (KBr pellets, cm^{-1}): $\nu(O-H)$, 3433 m (br); $\nu(C-H)$, 3054–2733w; $\nu(C=N)$, 1633s; $\nu(C-C_{arom})$, 1580–1498m. Anal. Calc. for $C_{22}H_{20}N_2O_2$: C, 76.72; H, 5.85; N, 8.13. Found: C, 76.78; H, 5.94; N, 8.20%.

2.3.2. α,α' -Bis(2-hydroxy-1-naphthalimino)-*m*-xylene (H_2L^2)

From *m*-xylylenediamine and 2-hydroxy-1-naphthalaldehyde. Yield, 97%. 1H NMR (500 MHz, $DMSO-d_6$, 25 °C, TMS): δ = 14.38

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