Compartmental Ligands: Synthesis and Characterization of Polynuclear Uranyl Complexes

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Abstract

The new compartmental ligand bis(salicylaldehyde)-2,6-dipicolinoylhydrazone (H_4L), was tested towards variable amounts of uranyl salts, giving rise to mono-, bi- and trinuclear uranyl complexes: $(H_2L)(UO_2)\cdot 2C_2H_5OH$, $L(UO_2)_2\cdot 4H_2O$ and $L(UO_2)_2\cdot 4H_2O(UO_2)(OCOCH_3)_2$. The different modes of ligation around the uranyl ions are tentatively discussed by comparison of their ^1H NMR and IR spectra.

Introduction

In the past few years a number of binucleating ligands, 'Compartmental Ligands', have been reported [1], having available adjacent, similar or dissimilar coordination compartments. These compounds can be mainly derived from triketones, ketoacids and ketophenols and their Schiff bases. Some interesting results have been obtained from aroyl-hydrazones [2]. Taking into account that pentadentate aroylhydrazones are useful ligands towards uranyl ions [3, 4] in order to obtain either ionic or neutral soluble uranyl complexes, we synthesized the new ligand bis-salicylaldehyde-2,6-dipicolinoylhydrazone **I** as potential mono-, bi- and tri-nucleating ligand towards the uranyl ion.

Experimental

Reagents

Reagent-grade uranyl acetate dihydrate, uranyl nitrate hexahydrate (Fluka), salicylaldehyde (Carlo Erba) were used without further purification. 2,6-Dipicolinoyl-hydrazine was prepared by reaction of 2,6-dipicolinate dimethyl ester.

Physical Measurements

Infrared spectra (200–4000 cm^{-1}) were recorded for KBr pellets or anhydrous Nujol between KBr plates on a Perkin Elmer 580 B spectrophotometer. Proton NMR spectra at 80 MHz for solutions in 99.93% $^2H_6$-dimethylsulphoxide (C.E.A.) were carried out on a Varian FT-80A instrument.

C, H, N microanalyses were carried out by Mr. A. Berton of this Institute; uranium was determined gravimetrically as the tetraphenylarsonium salt of dioxobis(pyridine-2,6-dicarboxylato)uranium(VI) [5].

Preparation of the Ligand H_4L, I

To a solution of salicylaldehyde (1.32 g, 11 mmol) in absolute ethanol (40 cm^3) a suspension of 2,6-dipicolinoylhydrazine (1.052 g, 5.4 mmol) in the same solvent (50 cm^3) was added at 60 °C. The mixture was left to react at reflux for 3 h, then the white microcrystalline product was filtered, washed several times with hot ethanol (20 cm^3 portions) and dried *in vacuo* (1.970 g, 90.5% yield). *Anal.* Found: C, 62.59; H, 4.38; N, 17.22. $C_{21}H_{17}N_5O_4$ requires: C, 62.50; H, 4.25; N, 17.37%.

$C_{21}H_{15}N_5O_4(UO_2)\cdot 2C_2H_5OH$, II

To a solution of the ligand (0.403 g, 1 mmol) in a mixture of absolute ethanol: pyridine (60:40; v:v) (40 cm^3), an ethanolic solution (20 cm^3) of uranyl acetate dihydrate (0.432 g, 1 mmol) was added, and the resulting mixture, containing an orange product, stirred at room temperature for 18 h. The product was filtered, washed several times with absolute ethanol and dried *in vacuo* (0.720 g; 92% yield). *Anal.* Found: C, 39.45; H, 3.70; N, 9.30; U, 31.50. $C_{25}H_{27}N_5O_8U$ requires: C, 39.32; H, 3.54; N, 9.17; U, 31.19%.

$C_{21}H_{13}N_5O_4(UO_2)_2\cdot 4H_2O$, III

(a) Preparation from II

To the complex **II** (0.580 g, 0.760 mmol), suspended in absolute ethanol (30 cm^3), a solution

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of uranyl nitrate hexahydrate (0.702 g, 1.39 mmol) in the same solvent was slowly added, and the resulting mixture refluxed for 3 h. The brownish-orange product formed was filtered, washed with portions of hot ethanol and dried *in vacuo* (0.758 g, 87% yield). *Anal.* Found: C, 25.25; H, 2.35; N, 6.90; U, 46.95. $C_{21}H_{21}N_5O_{12}U_2$ requires: C, 24.91; H, 2.09; N, 6.92; U, 47.07%.

(b) From H_4L *and* $UO_2(OCOCH_3)_2\cdot 2H_2O$

To a solution of the ligand (0.403 g, 1 mmol) in a mixture of absolute ethanol: pyridine (60:40; v:v) (40 cm^3) an ethanolic solution of uranyl acetate dihydrate (1.08 g, 2.6 mmol) was added, and the mixture stirred at 60 °C for 3 h. The brownish-orange product was filtered, washed several times with portions of hot ethanol and dried *in vacuo* (0.650 g, 75% yield).

$C_{21}H_{13}N_5O_4(UO_2\cdot 2H_2O)UO_2(OCOCH_3)_2$, *V*

(a) From II

To the suspension of **II** (0.580 g, 0.760 mmol) in absolute ethanol (40 cm^3), a solution of uranyl acetate dihydrate (3.22 g, 7.6 mmol) was slowly added at room temperature. Then the mixture was refluxed for 3 h and the orange-red product precipitated, was separated by filtration, washed with hot ethanol portions and dried *in vacuo* (0.776 g, 73% yield). *Anal.* Found: C, 21.75; H, 2.15; N, 4.85; U, 51.95. $C_{25}H_{27}N_5O_{18}U_3$ requires: C, 21.44; H, 1.94; N, 5.00; U, 51.03%.

(b) From the Ligand H_4L

Solid ligand H_4L (0.403 g, 1 mmol) was added to a refluxing solution of uranyl acetate dihydrate (4.24 g, 10 mmol) in ethanol (80 cm^3). After the first additions the ligand dissolved, with formation of an orange solution. When about half of the ligand had been added, an orange-red product began to precipitate. The mixture was refluxed for an additional 3 h and the product filtered, washed with ethanol and dried *in vacuo* (1.149 g, 81% yield).

$C_{21}H_{13}N_5O_4(UO_2\cdot 2DMSO)_2$, *IV*

(a) From III

The complex **III** (0.505 g, 0.5 mmol) was dissolved in DMSO (20 cm^3) at 80 °C, and the solution was stirred for 1 h. The solution was left at room temperature overnight, then ethanol (40 cm^3) was added affording red crystals. The product was filtered, washed several times with ethanol and dried at 80 °C *in vacuo* for 6 h. *Anal.* Found: C, 27.45; H, 2.60; N, 5.85; S, 10.70; U, 38.60. $C_{29}H_{37}N_5O_{12}S_4U_2$ requires: C, 27.80; H, 2.98; N, 5.59; S, 10.25; U, 38.03%.

(b) From II

By dissolving **II** (0.760 g, 1.0 mmol) in DMSO (25 cm^3) at room temperature, the formation of a white product is observed. The product isolated by filtration (0.240 g) was identified as H_4L by its ^1H NMR. To the filtered solution, ethanol (40 cm^3) was added at 80 °C. From the cooled solution, red crystals separated, which were isolated as reported above.

$C_{21}H_{43}N_5O_4(UO_2\cdot 2DMSO)_2(UO_2(OCOCH_3)_2)$, *VI*

(a) From V

The complex **VI** was isolated by crystallization in DMSO:EtOH (1:3; v:v) of the compound **V**.

(b) From IV

To a solution of **IV** (0.440 g, 0.392 mmol) in DMSO (20 cm^3), uranyl acetate dihydrate (0.424 g, 1 mmol) in DMSO solution was added. The solution was stirred at 80 °C for 3 h, then ethanol (20 cm^3) was added, giving a red product which was isolated following the usual method. *Anal.* Found: C, 23.85; H, 2.50; N, 4.70; S, 7.30; U, 44.00. $C_{33}H_{43}N_5O_{18}S_4U_3$ requires: C, 24.15; H, 2.64; N, 4.27; S, 7.82; U, 43.55%.

Results and Discussion

The ligand (H_4L) can act, in principle, as dianionic or tetra-anionic ligand due to the presence either of the phenolic and of the hydrazonic deprotonable hydrogens. The free rotation around the single bonds gives flexibility to the molecule and the ligand may coordinate with the uranyl ions in different modes (Fig. 1):

(a) as tri-dentate in the compartments defined by the aroylhydrazonic carbonyls and the phenolic groups **a**.

(b) in the compartments **a** and/or in the central one defined by the pyridyl-nitrogen and the two carbonyls **b**.

(c) as bridging some other ligand molecules.

Scheme 1 summarizes the reactions of the ligand (H_4L) with the uranyl salts in different molar ratios and the transformations which the various compounds undergo.

On the basis of the results obtained, the ligand (H_4L) seems to use the coordination arrangements

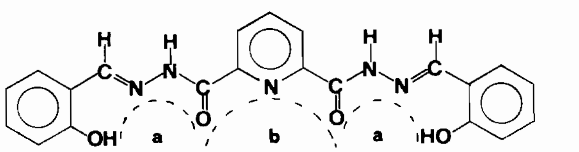
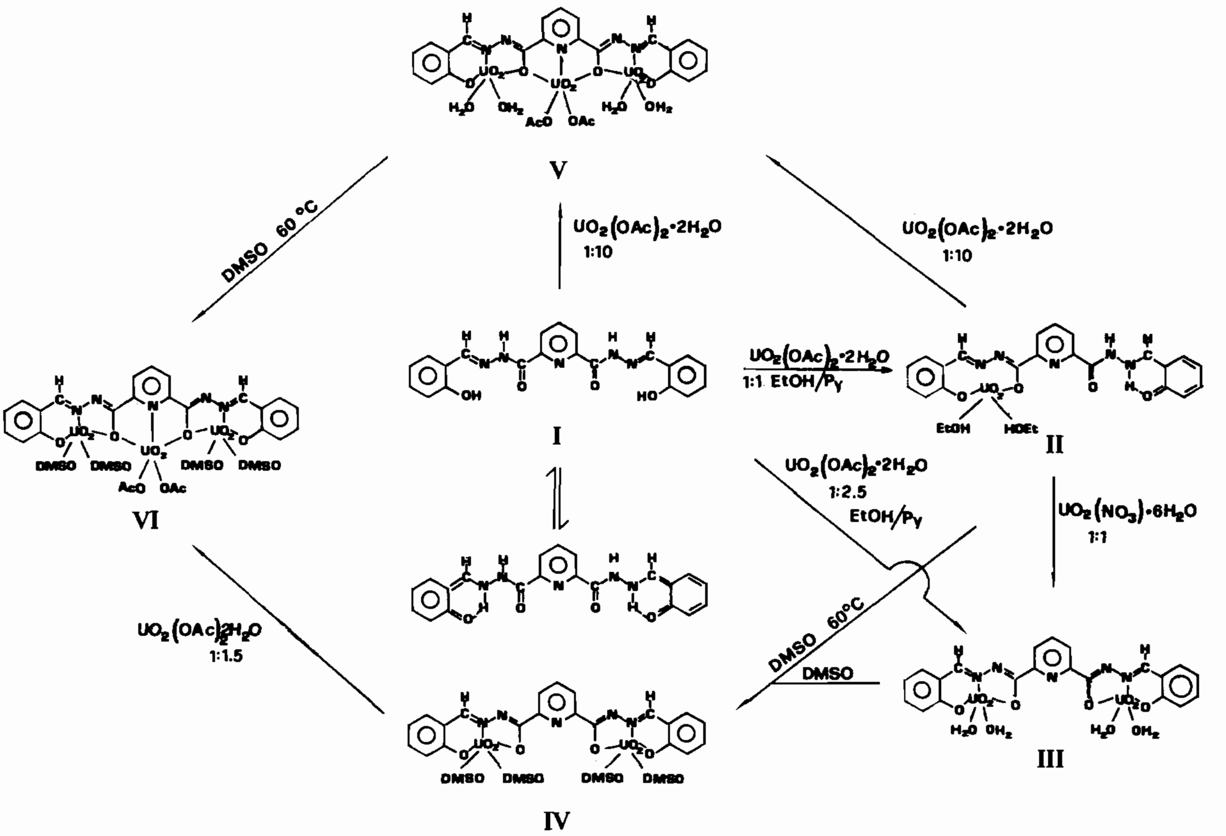


Fig. 1. The different coordinative compartments (a) and (b) of the ligand H_4L.



Scheme 1.

a and b of Fig. 1. Due to the low solubility of the complexes in the common organic solvents, the ^1H NMR spectra were carried out in DMSO-d_6 solutions. However it is known that DMSO is a strong neutral ligand towards the uranyl ion [6], and the substitution of the other neutral ligands coordinated to the uranyl has been observed. In the case of the complex **II** the dissolution into DMSO at 80 °C makes a re-distribution of the ligands according to the reaction:

$$2(H_2LUO_2\cdot 2C_2H_5OH) \xrightarrow[-2C_2H_5OH]{\text{DMSO, 60 °C}} L(UO_2)_2\cdot 4DMSO + H_4L$$

By treating the mononuclear species **II** with uranyl nitrate in molar ratio 1:2.5, the second compartment **a** is occupied by a second uranyl ion **III**. The same product **III** is obtained from the ligand and uranyl acetate in the molar ratio 1:2.5. The reaction of **III** with DMSO affords **IV** where all the coordinated water molecules are substituted by DMSO.

The entrance of the third uranyl ion into the **b** compartment may be realized either from the free ligand and the mononuclear species **II** by reaction with an excess of uranyl acetate, or from the binuclear species **III** and **IV** and uranyl acetate in molar ratio 1:1.5.

The reaction of **II** with uranyl nitrate to produce **III** with loss of HNO_3 is a further confirmation of the very high stability of these chelated uranyl systems towards acidic media [2].

Infrared Spectra

The infrared spectra (KBr pellets or Nujol mulls) of the free ligand show the presence, in the $\nu(C{=}O)$ stretching region, of two equally intense absorption bands at 1700 cm^{-1} and 1685 cm^{-1}, which suggest strongly that the ligand is present in the tautomeric form **I**, (Fig. 2).

In the mononuclear complex **II**, an increase in the intensity of the band centered at 1615 cm^{-1}, due to the C=N–N=C residue [2, 7] can be observed together with the bands due to $\nu(NH)$ at 3305 and 3276 cm^{-1}, and a reduction in intensity of the $\nu(C{=}O)$ at 1700 and 1685 cm^{-1}. The $\nu_{as}(UO_2)$ falls at 925 cm^{-1}, in good agreement with the data obtained for analogous aroylhydrazonato systems [2, 3].

On the other hand, the spectra of the binuclear species **III** have neither the absorption bands due

TABLE I. ^1H NMR Data (DMSO-d_6) of the Ligand and the Complexes.

Compound	(ppm from TMS)
H_4L, I	12.41 (s, 2H, O*H*); 11.06 (s, 2H, N*H*); 8.95 (s, 2 H, C*H*=N–); 8.35 (m, 3H, AB_2 pyrid.); 7.27 (m, 8H, AA'BB', phen. prot.)
$LUO_2 \cdot 2C_2H_5OH$, II	12.36 (s, 2H, O*H*); 11.06 (s, 2H, N*H*); 9.37 (s, 2 H, C*H*=N–); 8.84–6.64 (m, 33 H, phen. and pyr. prot.); 3.40 (q, 4H,–C*H*$_2$– CH_3, J = 7 Hz); 1.06 (t, 6H, CH_3–, J = 7 Hz).
$L(UO_2)_2 \cdot 4H_2O$, III	9.36 (s, 2 H, C*H*=N–); 8.35 (m, 3H, AB_2 pyr.); 7.15 (m, AA'BB', phen. prot.); 3.40 (s, 6H, H_2O).
$L(UO_2 \cdot 2DMSO)_2(UO_2(OCOCH_3)_2)$, VI	9.36 (s, 2H, C*H*=N–); 8.83 (m, 3H, AB_2 pyr.); 7.15 (m, 8H, AA'-BB' phen. prot.) 2.74 (s, 24H, DMSO); 3.57 (s, 6H, C*H*$_3$–COO).

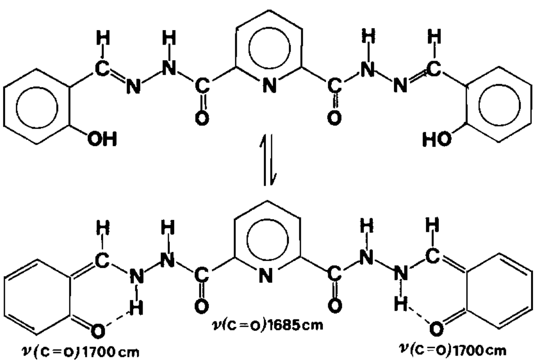


Fig. 2. The tautomeric keto-enol equilibrium of the ligand, as detected by its IR spectrum.

to ν(NH) stretching or the amide I band ν(C=O), but shows the same strong absorption band at 1617 cm^{-1}, while the unique $\nu_{as}(UO_2)$ is at 940 cm^{-1}. The binuclear species **IV** shows, in addition to the above described bands, an additional strong band at *ca.* 1000 cm^{-1}, due to the coordinated DMSO.

The spectra of the trinuclear species **V** and **VI** parallel those of the binuclear complexes, the only differences being due to the presence of two strong absorption bands at 945 and 917 cm^{-1} in an approximate ratio of 2:1, which can be assigned to the asymmetric stretchings of the two uranyl groups in different environments [8] and the absorption bands related to the acetato groups. The coordination mode of the acetato groups cannot be unambiguously assigned since some ligand absorption bands are present in the same range.

^1H NMR

As previously mentioned, the low solubility of the complexes forced us into using DMSO-d_6 as solvent. Due to the coordinative force of DMSO the following discussion of the ^1H NMR data concerns only the **IV** and **VI** species. The proton NMR spectra (DMSO-d_6) of **III** and **IV** confirms the lack of the OH and NH protons observed in their IR spectra. The presence of only one set of signals suggests a symmetric structure for this complex, and the diamagnetic shift of the protons close to the coordinated atoms is indicative of the coordination mode of the ligand. Thus the aldiminic protons, which, in the free ligand fall at δ 8.95, are shifted downfield to δ 9.37 ($\Delta\delta$ = 0.42), and a minor shift ($\Delta\delta$ = 0.12) is observed for the phenyl protons, while the pyridine protons appear unchanged. The last behaviour is convincing that the two uranyl ions are chelated into compartment **a**.

On the other hand the spectra of the species **V** and **VI**, in addition to the above mentioned resonances assignable to the chelation of the two uranyl ions into the sites **a**, show the signals due to the AB_2 pyridine system shifted downfield to δ 8.83 ($\Delta\delta$ = 0.48), thus indicating that the third uranyl ion is coordinated into compartment **b**.

As far as the ^1H NMR spectrum (DMSO-d_6) of **II** is concerned, it results in a superimposition of two distinct spectra due to the species **IV** and to the free ligand according to the rearrangement reaction 1. The assignments of the number of neutral coordinated molecules were carried out either by ^1H NMR or by thermogravimetric measurements.

Some preliminary results on the use of the new ligand in the synthesis of polynuclear complexes with transition metals (Ni^{II}, Zn^{II}, Cu^{II}) suggest some interesting outlooks in this field.

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