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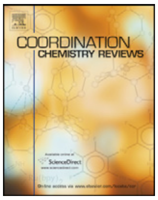

Review

A new chelate ligand designed for the uranyl ion

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Contents

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ABSTRACT

The ligand L, L = N,N′-di(2-hydroxy-4,6-di-*tert*-butyl-benzyl)imidazolidine, reacts with UO_2^{2+}, in organic and aqueous media, to yield a complex of UO_2^{2+} with the ligand L′, L′ = N,N′-di(2-hydroxy-4,6-di-*tert*-butyl-benzyl)-N-2-hydroxylethane–ethylenediamine. The opening of the imidazolidinic ring is a base catalyzed process which is induced by the uranyl ions. The complex $UO_2^{2+}L'$ has two reasonably strong absorption bands at 390 and 490 nm. Thus L can be used to determine quantitatively the concentration of UO_2^{2+} in protic and aprotic media.

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1. Introduction

The worldwide need for a non-polluted clean environment stimulates the global efforts to develop new sensitive sensors for polluting waste e.g. uranyl ions. As such extensive studies have been dedicated to the aim of developing new sensitive and selective spectrophotometric reagents and improving existing procedures [1–15], in order to develop simple and accessible procedures for the analysis of the cation. Spectrophotometric determinations will reduce the need to apply techniques that require expensive equipment with higher operation costs such as inductively coupled plasma atomic emission spectrometry [16], inductively coupled plasma–mass spectrometry [17,18], neutron activation analysis, gamma and alpha spectrometry. The hard acid, though relatively large uranyl cation is expected to form stable complexes with diamino tetra-dentate dianionic open chain ligands [19–24]. Complexes with phenolate ligands are expected to have LMCT bands hopefully in the visible region. As the two axial positions of the dioxo cation are occupied it was decided to design a flexible ligand, which will be able to adjust itself to the coordination demands of the central metal ion in the equatorial plane. Herein we report of a new chelate agent for the uranyl cation – N,N′-di(2-hydroxy-4,6-di-*tert*-

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butyl-benzyl)imidazolidine – L. The reaction of L with the uranyl ion involves the opening of the imidazolidine ring to yield a complex of the type UO_2L', L′ = N,N′-di(2-hydroxy-4,6-di-*tert*-butyl-benzyl)-N-2-hydroxylethane–ethylenediamine. An immediate deep color change is observed upon complex formation and a red solution with two characteristic absorption bands is obtained. The results point out that this ligand can be used as a reagent for the determination of the uranyl ion in aqueous and non-aqueous solutions, in 1 cm cells, in the 2.5×10^{-5} M to 7.5×10^{-4} M concentration range, or as a colorimetric sensor for determining the presence of uranyl ions in solutions.

2. Experimental

2.1. Materials

All the chemicals used were of AR grade and were used without further treatment. All solutions were prepared with de-ionized water, which was further purified by passing through a Millipore Milli-Q water purification system, the final resistance being above $10\,M\Omega\,cm^{-1}$.

The uranyl solutions were prepared from $(UO_2)(NO_3)_2 \cdot 6H_2O$ salt (assay: 99%, Merck), a standard stock of 1.0×10^{-3} M solutions was prepared by dissolving the appropriate amount of the salt and diluting to the mark (100 mL) with water or acetonitrile. pH adjustments were performed with NaOH and $HClO_4$ solutions. The pH in solutions in the acetonitrile:water solvent mixtures was measured by immersing the electrode in the medium.

2.2. Instrumentation

All UV–vis measurements were performed using a Hewlett Packard 8452 diode array spectrophotometer. ^1H and ^{13}C NMR spectra were recorded in CD_3CN or $CDCl_3$ at 200 and 500 MHz using Bruker Advance DMX 500 or Bruker Advance DPX 200 spectrometers.

Microanalysis was performed by the laboratory of microanalysis of the Hebrew University of Jerusalem.

2.3. Synthesis and spectroscopic data of the ligand

The free ligand L was prepared according to the following procedure. To 2.4 mL (0.036 mol) of ethylenediamine in 50 mL of methanol 9.6 mL (0.108 mol) of formaldehyde (37% solution) was added. The reaction mixture was refluxed for 3 h. 2,4-di-*tert*-butylphenol (15 g, 0.072 mol) in methanol (50 mL) was added to the solution. The mixture was refluxed for 12 h and allowed to cool to room temperature. A white precipitate was isolated, washed in ethanol and dried under vacuum. 70% yield was obtained. The ligand is nearly insoluble in water.

Elemental analysis calculated for $(C_{33}H_{52}N_2O_2)$ C, 77.95; H, 10.24; N, 5.51. Found: C, 77.87; H, 10.38; N, 5.52.

2.3.1. Solution-state NMR spectra of L

^1H ($CDCl_3$): δ (ppm) 1.3 (18H, s); 1.5 (18H, s); 3.1 (4H, s); 3.5 (2H, s); 3.9 (4H, s); 6.8 (2H, d); 7.2 (2H, d).

^{13}C ($CDCl_3$): δ (ppm) 29.7, 31.7, 34.2, 34.9, 51.8, 59.3, 74.4, 120.9, 123.1, 123.3, 135.7, 140.8, 154.1.

Due to rapid topomerization on the NMR time scale, protons with identical constitution show chemical shift equivalence. The ^1H NMR spectrum of the ligand shows seven peaks. The two protons of the diastereotopic *t*-butyl groups appear as singlets with identical integration at 1.3 and 1.5 ppm. The ethylenic protons appear as a singlet at 3.1 ppm. The two protons on the bridging carbon are low field shifted as expected, and appear as a singlet at 3.5 ppm. The benzylic protons of the pendant arm give rise to a singlet at 3.9 ppm. There are two peaks in the aromatic part of the spectrum at 6.8 and 7.2 ppm with characteristic meta splitting patterns ($J^4_{(meta)} = 2.4$ Hz), while the proton closer to the imidazolinic amine should be low field shifted. In the ^{13}C NMR spectrum there are 13 peaks, the lowest field resonance is assigned to the carbon of the aromatic ring substituted with a hydroxyl group. The highest field resonances at 29.7 and 31.7 ppm are of the *tert*-butyl groups.

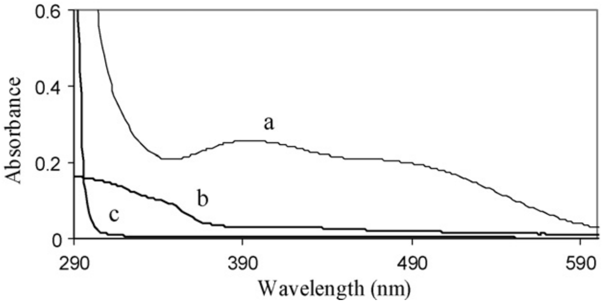


Fig. 1. Characteristic absorption spectra. Conditions: 1.0×10^{-4} M UO_2^{2+}, 3×10^{-4} M L (a), 1×10^{-4} M UO_2^{2+} (b), 3×10^{-4} M L (c), pH 4.5, acetonitrile:water 17:3.

3. Results and discussion

3.1. Characterization of the interaction of L with the uranyl cation

In order to examine the interaction of the uranyl ion with the ligand, a solution containing both reagents in a 17:3 acetonitrile:water volumetric ratio was prepared by mixing measured aliquots of an aqueous solution of uranyl nitrate and an acetonitrile solution of L. Absorption spectra of L, $UO_2(NO_3)_2$ and of a solution containing both reagents are plotted in Fig. 1 (note that NO_3^- contributes to the absorption at $\lambda < 320$ nm). Comparison of the three spectra in the visible region shows a significant change of the characteristic absorption spectra, indicating the formation of a complex. The complex has two characteristic absorption bands at 394 and 480 nm, in the water acetonitrile solvent mixture. During the investigation of the complex formation process, it was observed that the process is relatively slow both in the ethylacetate acetonitrile system (Fig. 2), and in the water acetonitrile system (Fig. 3). Since the reaction rate is too slow for a ligand exchange reaction it seemed reasonable to assume that the complexation facilitates the opening of the imidazolidine ring [25] (Scheme 1) in a base catalyzed reaction as can be seen from the effect of adding triethylamine to the ethylacetate

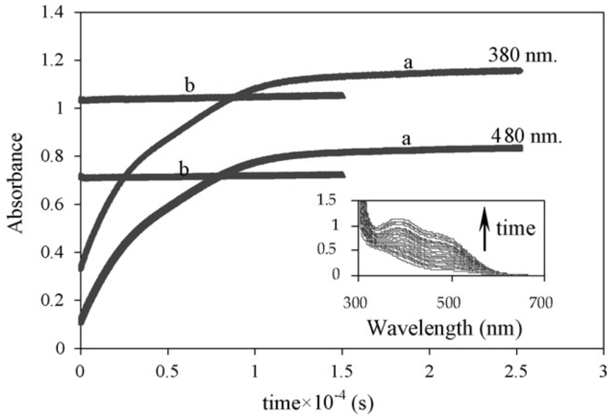


Fig. 2. Effect of a base on the kinetics of the complex formation. Conditions: 4.0×10^{-4} M UO_2^{2+} (a, b), 1.0×10^{-2} M L (a, b), ethylacetate:acetonitrile: 3.5 : 2.5 (a, b), 3×10^{-3} M triethylamine (b) $\lambda = 380$, 480 nm. Insert: spectra measured during the kinetics of the complex formation (a).

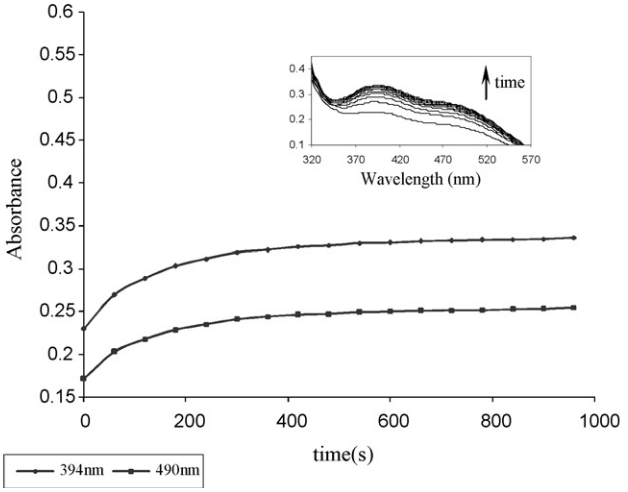


Fig. 3. The kinetics of complex formation. Conditions: 3×10^{-4} M $UO_2(NO_3)_2$, 7.5×10^{-4} M L, acetonitrile:water 17:3 vol. ratio, pH 4.5. Insert: spectra measured during kinetics of the complex formation.

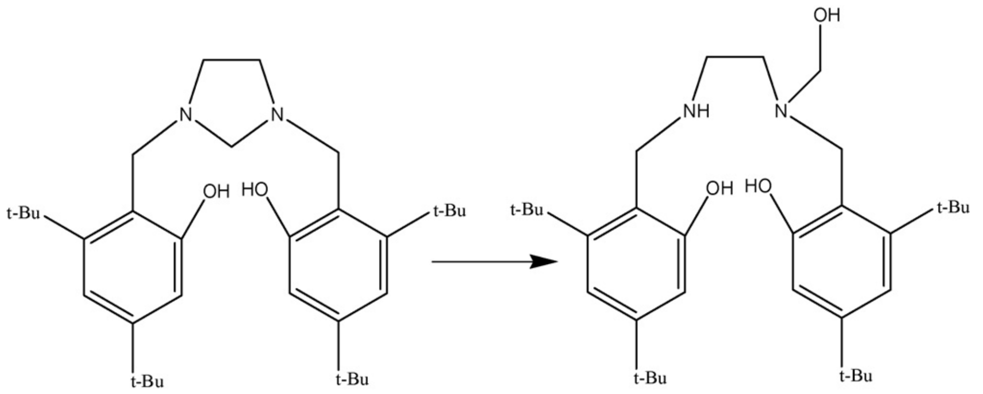
acetonitrile solvent mixture (Fig. 2). NMR experiments confirmed this assumption; Fig. 4 shows the difference in the ^{13}C NMR spectra of the ligand due to the complex formation. In this experiment the complex was formed in CD_3CN, and then a drop of hydrochloric acid was added to reverse the complex formation, in order to determine the structure of the transformed ligand (spectrum B in Fig. 4); the four peaks at 29.9, 30.3, 31.5 and 31.7 ppm are assigned to the methyl residues of the *t*-butyl groups on the aromatic rings. The four quaternary carbon atoms of these groups appear at 35.1, 35.2, 35.5, and 35.6 ppm. The peak at 49.2 ppm is attributed to the carbon of the ethylenediamine bond that is distanced from the hydroxyl group that was added with the opening of the imidazolidine ring, the second carbon is shifted to lower field and appears at 51.9 ppm. The two carbon atoms on the ligand arm appear at 43.2 and 49.6 ppm as expected the carbon closer to the added hydroxyl group is low field shifted. The peak at 80 ppm is attributed to the carbon of the new hydroxyl group. The peaks at 115.1, 121.6, 123.3, 125.0, 126.8, 127.8, 138.7, 140.6, 145.2, 146.9, 148.3 and 152.1 ppm are assigned to the aromatic carbon atoms. The carbon atoms of the aromatic ring substituted with the hydroxyl groups appear at lower field. The transformation in the ligand structure is attributed to the decrease in the electron density on the imidazolidinic nitrogen atoms coordinated to the Lewis acid uranyl ion, thus weakening the nitrogen–carbon bond and enabling the nucleophilic attack in a base catalyzed reaction and the complex is formed with the transformed ligand (L′). The base attacking the imidazolidinic nitrogen is either OH^- or $UO_2(OH)^+$ present in the solution. No transformation of the ligand structure occurs in the absence of the uranyl cation.

3.1.1. Solution-state NMR spectra of the uranyl–L′ complex

The ^{13}C NMR spectrum of the complex has the same number of peaks as the open ligand. However, the complex formation increases the rigidity of the ligand structure, as a result the *t*-butyl carbon atoms are almost identical (29.6, 30.2, 31.6, 32.0 ppm) and also the peaks of the aromatic carbon atoms are less separated (120.8, 121.6, 123.0, 123.3, 123.8, 123.9, 135.6, 135.9, 140.6, 140.7, 154.0, 154.4 ppm), i.e. the uranyl ion has increased the symmetry of the coordinated ligand.

3.1.2. Spectrophotometric determination of the complex stoichiometry

In order to determine the complex stoichiometry two spectrophotometric methods have been used: the method of continues



Scheme 1. Opening of the imidazolidine ring due to the complex formation.

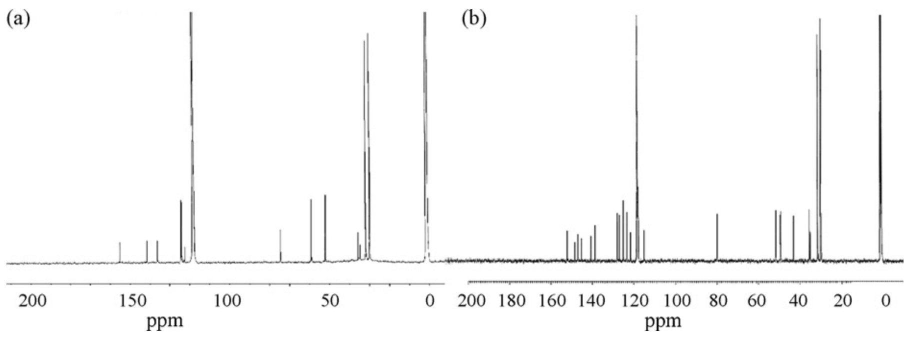


Fig. 4. Change in the ^{13}C NMR (CD_3CN) spectrum of the ligand due to imidazolidine ring opening. Conditions: ^{13}C NMR spectrum of L^1 (a), spectrum of a complex solution that was acidified a day after the complex preparation, with HCl, to obtain the free transformed ligand, 1×10^{-3} M UO_2^{2+}, 1.0×10^{-3} M L (b).

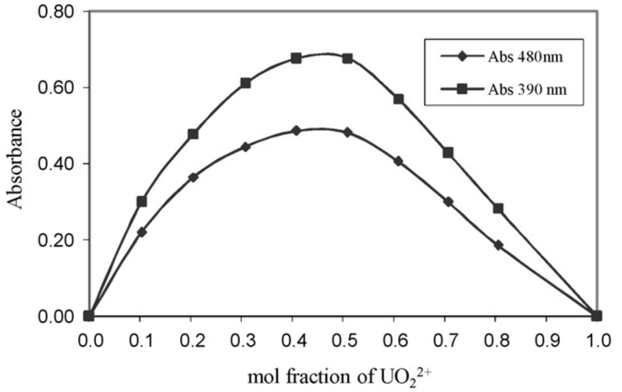


Fig. 5. Determination of the complex stoichiometry; method of continuous variation. Conditions: ($[UO_2^{2+}] + [L]) = 4.0 \times 10^{-3}$ M, ethylacetate:acetonitrile 3.5:2.5, spectra were taken a day after preparation.

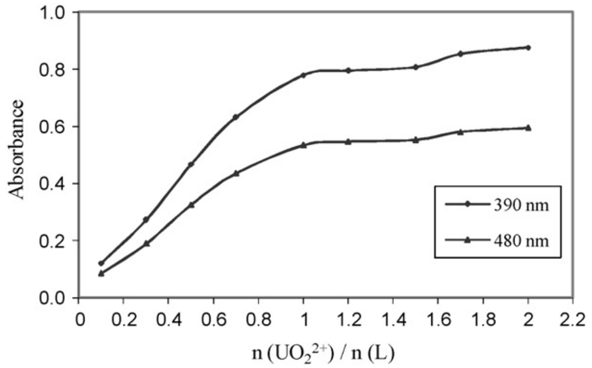


Fig. 6. Determination of the complex stoichiometry; the mole ratio method. Conditions: 1.00×10^{-3} M L, $(0.10–2.00) \times 10^{-3}$ M UO_2^{2+}, ethylacetate:acetonitrile 3.5:2.5, spectra were taken a day after preparation.

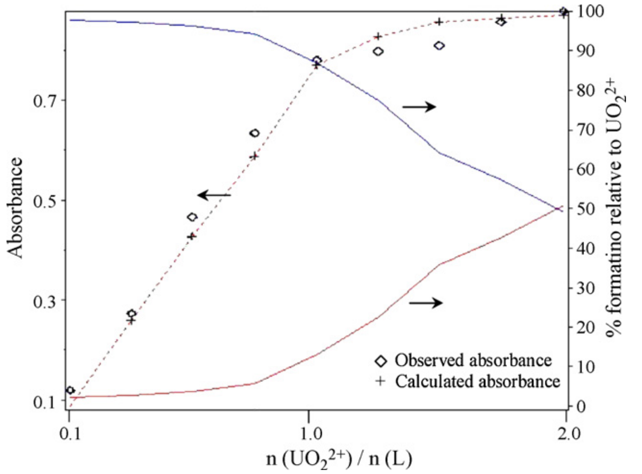


Fig. 7. Determination of the equilibrium constant of the complex formation applying the "HYPERQUAD 2006" program. Conditions: 1.00×10^{-3} M L, 0.10×10^{-3} M to 2.00×10^{-3} M UO_2^{2+}, ethylacetate:acetonitrile 3.5:2.5, spectra were taken a day after preparation (the plot is an output of *K* as calculated by the "HYPERQUAD 2006" program).

variation (Fig. 5) and the mole ratio method (Fig. 6). Both experiments indicate that a 1:1 complex is formed.

The apparent stability constant of the complex in the ethylacetate acetonitrile mixture, $\log K = 4.7 \pm 0.2$ was evaluated applying the "HYPERQUAD 2006" program [26]. A calculation assuming the formation of ML_2 failed to converge (Fig. 7).

During the investigation of the interaction between the ligand and the uranyl cation in the water acetonitrile solvent mixture a clear dependence on the pH and acetonitrile:water volumetric ratio was observed. In order to examine these dependencies three sets of spectrophotometric measurements were performed for solutions containing a constant excess of L. In each one a constant volumetric ratio of acetonitrile:water was kept (19:1, 18:2, 17:3), while in each

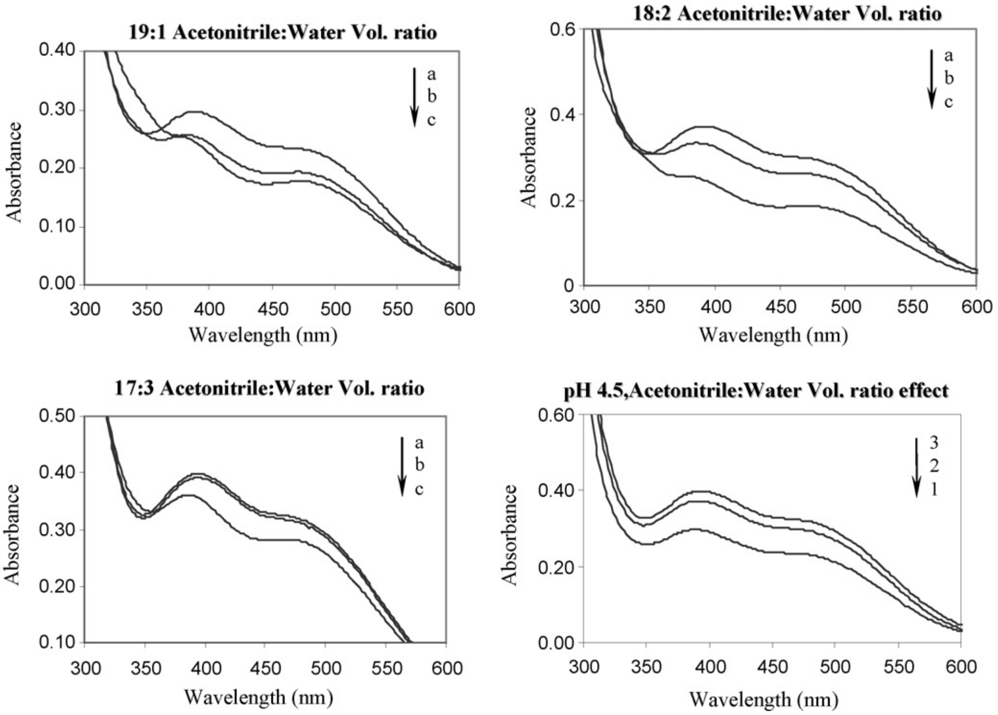


Fig. 8. pH and acetonitrile:water volumetric ratio effects on complex formation. Conditions: all solutions contained 1.3×10^{-4} M $UO_2(NO_3)_2$, 7.5×10^{-4} M L, acetonitrile:water volumetric ratio 19:1 (series **1**), 18:2 (series **2**), 17:3 (series **3**), **pH**; 4.5 (a), 5.0 (b), 5.5 (c).

Table 1
Calibration data for spectrophotometric analysis of uranyl.

$[UO_2^{2+}]$ (M)	Ethylacetate–acetonitrile solvents mixture (**a**)				Acetonitrile–water solvents mixture (**b**)			
	Absorption at 380 nm (average)	%R.S.D.	Absorption at 480 nm (average)	%R.S.D.	Absorption at 394 nm (average)	%R.S.D.	Absorption at 480 nm (average)	%R.S.D.
2.50×10^{-5}	0.080	8.0	0.043	2.0	0.0853	6.3	0.072	6.6
5.00×10^{-5}	0.156	4.6	0.088	5.0	0.165	2.3	0.133	3.4
6.00×10^{-5}	0.193	3.5	0.110	3.8	–	–	–	–
7.50×10^{-5}	0.234	4.4	0.129	4.9	0.239	1.4	0.194	3.3
1.00×10^{-4}	0.318	4.2	0.182	3.7	0.315	1.8	0.253	3.1
1.50×10^{-4}	–	–	–	–	0.435	0.81	0.347	1.5
2.50×10^{-4}	0.808	1.9	0.498	2.2	–	–	–	–
3.75×10^{-4}	1.28	1.2	0.748	1.6	–	–	–	–
5.00×10^{-4}	1.62	0.89	0.988	2.1	–	–	–	–
7.50×10^{-4}	2.42	1.36	1.46	1.6	–	–	–	–

Conditions: (**a**) $(0.25–7.5) \times 10^{-4}$ M UO_2^{2+}, 1.5×10^{-2} M L, 3×10^{-3} M triethylamine, vol. ratio ethylacetate:acetonitrile 3.5:2.5. (**b**) $(0.25–1.5) \times 10^{-4}$ M $UO_2(NO_3)_2$; 2.4×10^{-2} M Tris acid, 1.5×10^{-3} M L, pH 5.0, acetonitrile:water volumetric ratio 17:3, $\lambda = 394$, 480 nm.

Table 2
Summary of the spectophotometric measurements: effect of the addition of Co^{2+} and Ni^{2+} ions to the ethylacetate–acetonitrile solvents mixture.

$[UO_2^{2+}]$ (M)	No additive		Ni^{2+}		Co^{2+}	
	Absorption at 380 nm (average)	%R.S.D.	Absorption at 380 nm (average)	%R.S.D	Absorption at 380 nm (average)	%R.S.D
2.50×10^{-5}	0.080	8.0	0.0715	2.0	0.0754	6.8
5.00×10^{-5}	0.156	4.6	0.156	5.0	0.149	4.1
6.00×10^{-5}	0.193	3.5	0.182	3.8	0.175	2.0
7.50×10^{-5}	0.234	4.4	0.233	4.9	0.219	3.5
1.00×10^{-4}	0.318	4.2	0.309	3.7	0.308	1.8
2.50×10^{-4}	0.808	1.9	0.818	2.2	0.795	0.86
3.75×10^{-4}	1.28	1.2	1.24	1.6	1.25	0.73
5.00×10^{-4}	1.62	0.89	1.67	2.1	1.69	1.1

Conditions: $(0.25–5.0) \times 10^{-4}$ M UO_2^{2+}, $(0.25–5.0) \times 10^{-5}$ M Ni^{2+}/ Co^{2+} (the concentration was always 10% of the $[UO_2^{2+}]$ for all experiments), 1.5×10^{-2} M L, 3×10^{-3} M triethylamine, ethylacetate:acetonitrile 3.5:2.5).

set the pH effect was examined. As can be seen in Fig. 8 the system is pH sensitive. The decrease in the absorption observed at pH 5.0 and 5.5 is due to the precipitation of sodium diuranate, although in the 17:3 volumetric ratio this decrease is less pronounced. It was thus decided that for the acetonitrile water solvent mixture, working in the 4.5–5.0 pH range and in 17:3 acetonitrile:water volumetric ratio is optimal.

3.2. A new spectrophotometric method for quantitative analysis of uranyl ion concentration

The immediate deep color change observed upon complex formation to obtain a red solution with two characteristic absorption bands in the visible region encouraged us to examine the possibility that this ligand can be used as a reagent for the spectrophotometric determination of the uranyl ion concentration in aqueous and non-aqueous solutions. Solutions were prepared by mixing measured aliquots of stock solutions of uranyl nitrate and L keeping a constant excess concentration of the ligand, and increasing the concentration of the uranyl cation. The experiments were performed both in the ethylacetate acetonitrile and in acetonitrile water solvent mixtures; a constant volumetric ratio was kept in both media. In the ethylacetate acetonitrile solvent mixture triethylamine was added to catalyze the complex formation. In the acetonitrile water solvent mixture a buffer was added, as the system is pH sensitive. The biological buffer Tris acid was used (pH adjusted to 5.0) in order to avoid the use of a buffer that can ligate to the uranyl ions and replace L′ in the coordination sphere. pH measurements were performed to ensure that the pH is in the desired range (4.5–5.0). The absorption of the solution was measured against the solvents blank and typical data for calibration curves (average of five repetitions) for both media are given in Table 1. The values of the percent of the standard deviation from the average were calculated.

The addition of foreign ions that might compete with the uranyl ion in coordinating to the ligand was examined. The addition of Ni^{2+} and Co^{2+} in both media and also $Fe^{III}{}_{aq}$ in the acetonitrile water solvent mixture, in a concentration of ten percent of the uranyl ion concentration was examined. The ligand concentration and the range of the uranyl concentration are the same as in the previous

Table 3
Summary of the spectophotometric measurements; effect of the addition of Co^{2+}, Ni^{2+} and $Fe^{III}{}_{(aq)}$ ions to the acetonitrile–water solvents mixture.

$[UO_2^{2+}]$ (M)	No additive		Ni^{2+}		Co^{2+}		Fe^{3+}	
	Absorption at 394 nm (average)	%R.S.D.	Absorption at 394 nm (average)	%R.S.D.	Absorption at 394 nm (average)	%R.S.D.	Absorption at 394 nm (average)	%R.S.D.
2.5×10^{-5}	0.0853	6.3	0.078	3.8	0.077	4.6	0.077	2.6
5.0×10^{-5}	0.165	2.3	0.155	2.6	0.159	3.6	0.158	0.32
7.5×10^{-5}	0.239	1.4	0.234	1.7	0.235	1.8	0.233	0.30
1.0×10^{-4}	0.315	1.8	0.302	1.2	0.305	1.9	0.304	1.0
1.5×10^{-4}	0.435	0.81	0.427	1.2	0.434	1.7	0.422	1.5

Conditions: $(0.25–1.5) \times 10^{-5}$ M Ni^{2+}/Co^{2+}/$Fe^{III}{}_{(aq)}$ (the concentration was always 10% of the $[UO_2^{2+}]$ for all experiments) 1.5×10^{-3} M L, 2.4×10^{-2} M Tris acid, acetonitrile:water 17:3, pH 5.0.

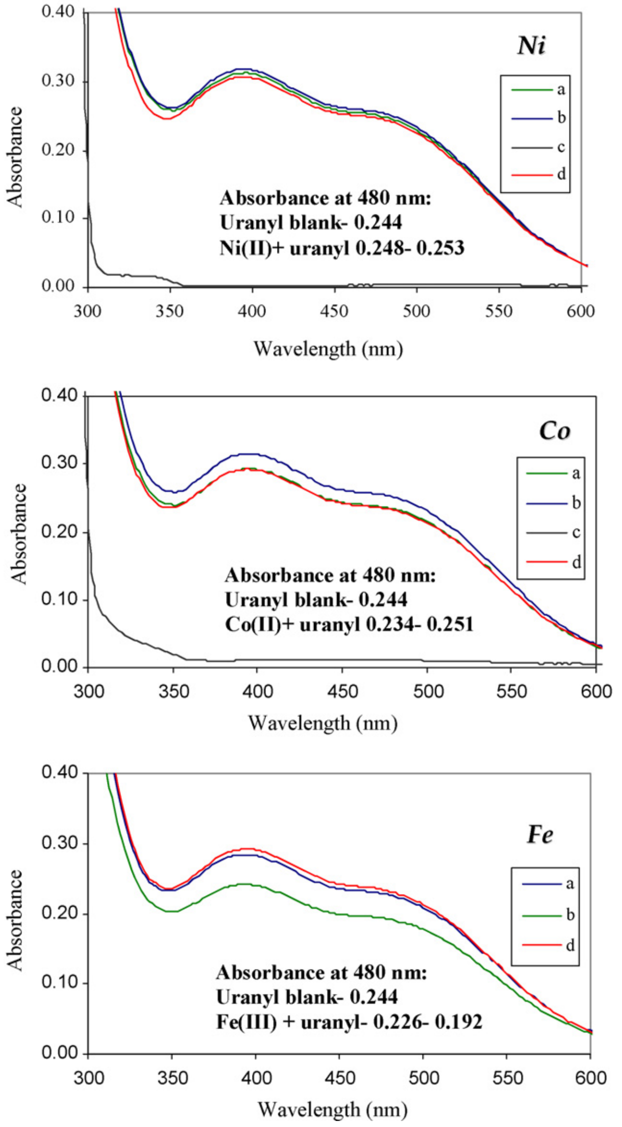


Fig. 9. Effect of increasing Ni^{2+}, Co^{2+} and $Fe^{III}_{(aq)}$ concentration. Conditions: 1.00×10^{-4} M UO_2^{2+}(a, b, d), 0.10×10^{-4} M $Ni^{2+}/Co^{2+}/Fe^{III}_{(aq)}$ (a), 1.0×10^{-4} M $Ni^{2+}/Co^{2+}/Fe^{III}_{(aq)}$ (b, c), 1.5×10^{-3} M L (a–d), 2.4×10^{-2} M Tris acid (a–d), acetonitrile:water 17:3, pH 5.0.

experiments. Tables 2 and 3 summarize the average absorbance values (five measurements) and calculations of the percent of standard deviation from the average (%R.S.D.) of the experiments. Thus the addition of these cations has a negligible effect in the concentration range examined.

In the acetonitrile water solvent mixture the effect of increasing the metal ion concentration relatively to the uranyl concentration was examined. At a certain uranyl and ligand concentration the Ni^{2+}, Co^{2+} and Fe^{III}_{aq} concentrations were changed in the concentration range of 10–100% of the uranyl concentration. The increase of these cations concentrations caused a deviation of up to 4.3% for Ni^{2+}, 4.1% for Co^{2+} and 20% for Fe^{III}_{aq}, as can be seen in Fig. 9 by comparing the spectra obtained at different cation concentrations (only the lowest and highest concentrations are shown), to the spectrum of a blank solution containing the ligand and uranyl nitrate. Also shown are the spectra of blank solutions containing Co^{2+} or Ni^{2+} cation and the ligand. The last two spectra imply that this ligand can be used as a colorimetric sensor for determining the presence of uranyl ions in solutions.

4. Concluding remarks

N,N′-di(2-hydroxy-4,6-di-*tert*-butyl-benzyl)imidazolidine, reacts with uranyl ion to yield a complex of uranyl with N,N′-di(2-hydroxy-4,6-di-*tert*-butyl-benzyl)-N-2-hydroxylethane–ethylenediamine. The complexation facilitates the opening of the imidazolidine ring in a base catalyzed reaction.

The complex formation is accompanied by an immediate deep color change in a pH sensitive system and the experimental results indicate that this easily synthesized ligand can be used as a reagent for the analysis of the uranyl concentration in aqueous and non-aqueous solutions or as a colorimetric sensor for determining the presence of uranyl ions in solution. The fact that the complex has two absorption bands at 390 and 480 nm is an important analytical advantage. High concentrations of ferric ion interfere with the suggested method in the water acetonitrile solvent mixture, however in the ethylacetate acetonitrile solvents mixture they are not expected to interfere due to their low solubility in these solvents.

The ligand has been compared to several other spectrophotometric reagents that have been suggested for the analysis of uranyl ion in aqueous and organic solutions; AzIII [1,2] “isoamethyrin” [3], 4-(2′-pyridylazo)resorcinol (PAR) [7,14], 1-(2-pyridylazo)-2-naphthol (PAN) [6], 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (bromo-PADAP) [5], p-carboxychlorophosnazo (CPApK) [13]. All these reagents are considerably more sensitive than L′ and enable a detection limits in the order of several μM, in a 1 cm cell. For example the CPApK reagent, which reacts with uranyl in acidic medium, is very sensitive. The addition of the surfactant polyvinyl alcohol (PVA), increases both the sensitivity and the stability of the uranyl complex thus formed, with a molar absorptivity of $2.72 \times 10^5\,M^{-1}\,cm^{-1}$.

However an important advantage of the proposed reagent is the deep color change that is immediately observed upon complex formation, as the reagent L′ itself has no absorption band in the visible region, which is not the case for other reagents (for example the AzIII reagent has a deep purple color and no change in the solution color is observed upon metal complexation). Also important are the facts that the complex has two well defined absorption bands, its synthesis is relatively simple and so is the analytical procedure.

The fact that the complexation process can be reversed by altering the pH, implies that the hydrophobic L′ can also be used as an extractant of uranyl ion from aqueous solution.

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References

[1] H. Rohwer, N. Rheeder, E. Hosten, Anal. Chim. Acta 341 (1997) 263.
[2] G.E. Collins, Q. Lu, Anal. Chim. Acta 436 (2001) 181.
[3] J.L. Sessler, P.J. Melfi, D. Seidel, A.E.V. Gordon, D.K. Ford, P.D. Palmer, C.D. Tait, Tetrahedron 6 (2004) 11089.
[4] M.N. Abbas, A.M. Homoda, G.A.E. Mostafa, Anal. Chim. Acta 436 (2001) 223.
[5] D.A. Johnson, T.M. Florence, Anal. Chim. Acta 53 (1971) 73.
[6] S. Shibata, Anal. Chim. Acta 22 (1960) 479.
[7] T.M. Florence, Y. Farrar, Anal. Chem. 35 (1963) 1613.
[8] K.K. Gupta, P.G. Kulkarni, G. Thomas, N. Varadarajan, R.K. Singh, M.K.T. Nair, Talanta 40 (1993) 507.
[9] Y. Hirano, Y. Ogawa, K. Oguma, Anal. Sci. 19 (2003) 303.
[10] A. Suresh, D.K. Patre, T.G. Srinivasan, P.R. Vasudeva Rau, Spectrochim. Acta A 58 (2002) 341.
[11] G. Kwapulinska, B. Janoszka, Fresenius, J. Anal. Chem. 338 (1990) 641.
[12] L.S.G. Teixeira, A.C.S. Costa, S.L.C. Ferreira, M.L. Freitas, M.S. Carvalho, J. Braz. Chem. Soc. 10 (1999) 519.
[13] Y. Ru, L. Yan, S. Guilan, W. Tao, P. Jiaomai, Anal. Chim. Acta 314 (1995) 95.
[14] L. Sommer, V.M. Ivanov, H. Novotna, Talanta 14 (1967) 329.
[15] L. Jancar, B. Slezackova, L. Sommer, Talanta 36 (1989) 549.

[16] O. Fujino, S. Umetani, E. Ueno, K. Shigeta, T. Matsuda, Anal. Chim. Acta 420 (2000) 65.
[17] J.G. Sen Gupta, N.B. Bertrand, Talanta 42 (1995) 1595.
[18] S. Joannon, P. Telouk, C. Pin, Spectrochim. Acta B 52 (1997) 1783.
[19] M.S. Bharara, K. Heflin, S. Tonks, K.L. Strawbridge, A.E.V. Gorden, Dalton Trans. 22 (2008) 2967.
[20] M.S. Bharara, K.L. Strawbridge, J.Z. Vilsek, T.H. Bray, A.E.V. Gorden, Inorg. Chem. 46 (2007) 8309.
[21] S.K. Sahu, V. Chakravortty, J. Radioanal. Nucl. Chem. 227 (1998) 163.
[22] C.C. Gatto, E. Schulz-Lang, U. Abram, Inorg. Chem. Commun. 6 (2003) 1001.
[23] A. Dalla Cort, L. Mandolini, G. Palmieri, C. Pasquini, L. Schiaffino, Chem. Commun. (2003) 2178.
[24] A.E.V. Gordon, J. Xu, K.N. Raymond, Chem. Rev. 103 (2003) 4207.
[25] V.M. Ugalde-Saldivar, H. Hopfl, N. Farfán, A.R. Toscano, M.E. Sosa-Torres, Inorg. Chim. Acta 358 (2005) 3545.
[26] P. Gans, A. Sabatini, A. Vacca, Talanta 43 (1996) 1739.