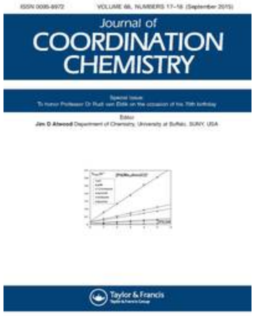


Journal of Coordination Chemistry

ISSN: 0095-8972 (Print) 1029-0389 (Online) Journal homepage: http://www.tandfonline.com/loi/gcoo20

Design of a ligand suitable for sensitive uranyl analysis in aqueous solutions

Yael Albo, Nina Buzaglo, Eric Maimon, Israel Zilbermann & Dan Meyerstein

To cite this article: Yael Albo, Nina Buzaglo, Eric Maimon, Israel Zilbermann & Dan Meyerstein (2015) Design of a ligand suitable for sensitive uranyl analysis in aqueous solutions, Journal of Coordination Chemistry, 68:17-18, 3079-3087, DOI: 10.1080/00958972.2015.1043287

To link to this article: http://dx.doi.org/10.1080/00958972.2015.1043287

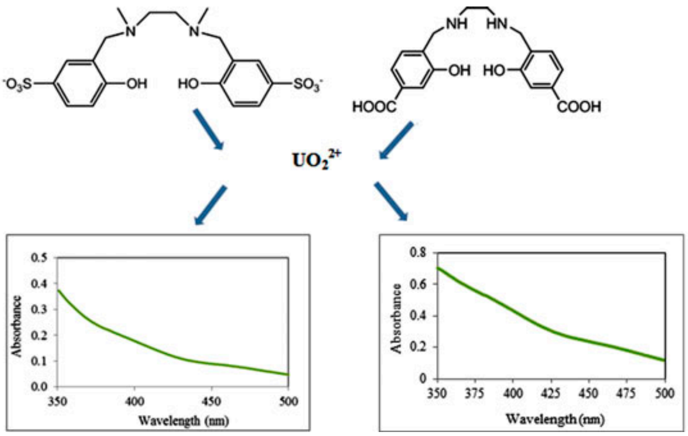
Journal of Coordination Chemistry, 2015
Vol. 68, Nos. 17–18, 3079–3087, http://dx.doi.org/10.1080/00958972.2015.1043287

Design of a ligand suitable for sensitive uranyl analysis in aqueous solutions

YAEL ALBO*†, NINA BUZAGLO‡, ERIC MAIMON‡§, ISRAEL ZILBERMANN‡§ and DAN MEYERSTEIN‡¶

†Chemical Engineering Department, Ariel University, Ariel, Israel
‡Chemistry Department, Ben-Gurion University of the Negev, Beer Sheva, Israel
§Chemistry Department, Nuclear Research Centre Negev, Beer-Sheva, Israel
¶Biological Chemistry Department, Ariel University, Ariel, Israel

(*Received 12 January 2015; accepted 2 April 2015*)



Several ligands were designed as plausible reagents for the spectrophotometric analysis of uranyl in aqueous solutions. The ligand L_3^{2-} = 3,3′-(ethane-1,2-diylbis(methylazanediyl))bis(methylene)bis(4-hydroxybenzenesulfonate) was found to fit best the requirements. The results point out that carboxylate substituents compete with the phenolate substituents as binding sites to the central uranium cation and therefore decrease the usefulness of ligands containing both carboxylate and phenolate substituents as analytical spectrophotometric reagents.

Keywords: Uranyl; Spectrophotometric analysis; Spectrophotometric reagent; Carboxylate substituents; Phenolate substituents

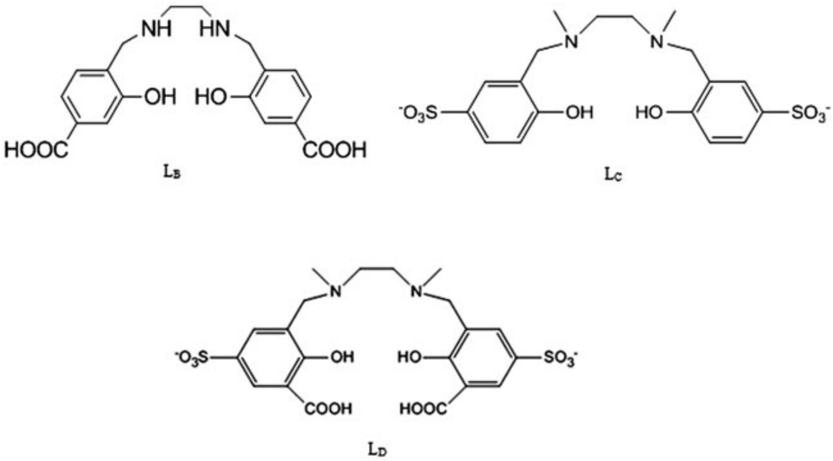
---

*Corresponding author. Email: yaelyt@ariel.ac.il
This article is dedicated to Professor Rudi van Eldik, a colleague and friend, upon his 70th birthday.

1. Introduction

Actinide chemistry is a subject of continuous interest due to the role of the actinides in the nuclear industry both in weapons and in energy production. Uranium is the key element in the nuclear industry. The production of the metal from mining of its ores involves large amounts of waste that increases the possibility of groundwater contamination. Design and synthesis of appropriate ligands that can be used for the analysis and extraction of the cation is essential for solving part of these problems and extensive studies have been dedicated to developing new sensitive and selective spectrophotometric reagents and improving existing procedures in order to develop simple and accessible procedures for the analysis of the cation [1–11] that will enable its detection in waste water.

Recently, it was reported [12] that L_A, L_A = N,N′-di(2-hydroxy-4,6-di-tert-butyl-benzyl) imidazoline, forms a complex with UO_2^{2+} with strong absorption bands in the visible and near UV region. These absorption bands were attributed to LMCT transitions from the phenolate groups to the central cation. The disadvantage of this ligand for analytical purposes is that the ligand and the complex are not soluble in aqueous solutions. It was therefore decided to synthesize the ligand L_B, L_B = ethane-1,2-diylbis(azanediyl))bis-(methylene) bis(3-hydroxybenzoic acid), with the hope that it will be water soluble. The results indeed prove that this ligand and its uranyl complex are water soluble, but the complex has no UV–vis absorption bands that enable analytical determination. Therefore, several potential mono-dentate phenolate ligands with different substituents were studied in order to determine the effect of the substituents on the spectrum of the complex. Based on the results, the ligands L_C^{2-}, L_C^{2-} = 3,3′-(ethane-1,2-diylbis(methylazanediyl))bis-(methylene)bis(4-hydroxybenzenesulfonate), and L_D^{2-}, L_D^{2-} = 5,5′-(ethane-1,2-diylbis(methyl-azanediyl))-bis(methylene)bis(3-carboxy-4-hydroxybenzenesulfonate) were synthesized (scheme 1). L_C indeed fits the requirements for a simple sensitive analysis of trace uranyl impurities in aqueous media, whereas the complex with L_D has considerably weaker absorption bands probably due to complexation by the carboxylates instead of the phenolates.



Scheme 1. Structures of L_B–L_D.

2. Experimental

2.1. *Materials and methods*

All the chemicals used in this study were of AR grade without any further purification. All the solutions were prepared with water, purified by a Milipore Milli-Q water purification system, final resistance >10 MΩ cm^{-1}. The uranyl solutions were prepared from $UO_2(NO_3)_2 \cdot 6H_2O$ salt (assay: 99%, Merck); a standard stock solution of 1.0×10^{-2} M was prepared by dissolving the appropriate amount of the salt and diluting to the required concentration with water. ^{1}H and ^{13}C NMR spectra were recorded in a Bruker spectrometer 400 MHz model DPX 500 MHz model DMX 500. UV–vis measurements were performed using an Agilent 8453 diode array spectrophotometer.

2.2. *Synthesis and characterization of the ligands*

Generally, the synthesis and ligand characterization was analogous to that of similar ligands [12].

2.2.1. Synthesis of L_B. To 4.0 g of ethylene-diamine (0.05 mol) in 100 mL ethanol, 10.0 g (0.1 mol) of formaldehyde (37% solution) was added. The mixture was stirred for 2 h and 15 g (0.1 mol) hydroxy-benzoic-acid was added, and the mixture was stirred at room temperature for 96 h. A white precipitate was obtained after addition of 10 mL of 0.1 M hydrochloric acid. Throughout the synthesis, the reaction vessel was covered with aluminum foil to prevent exposure to light. The reaction product was isolated, washed in ethanol, dried under vacuum and then recrystallized from 1 : 1 water : ethanol solution. L_B is soluble in water. ^{1}H (500 MHz, $CDCl_3$, 25 °C): δ(ppm) 3.10 (s, 4H, ethylenic bridge), 3.39 (s, 4H, benzylic pendant arm), 7.29 (d, 2H, aromatic), 7.34 (d, 2H, aromatic), 7.46 (dd, 4H, aromatic ortho to carboxylate), 8.01 (s, 2H, carboxylate protons). ^{13}C (500 MHz, $CDCl_3$, 25 °C): δ(ppm) 48.4 (pendant arm), 49.3 (ethylenic bridge), 120.3, 125.5, 129.5, 129.9, 155.1, 175.0 (aromatic carbons), 215.6 (C–OOH).

2.2.2. Synthesis of L_C. To 4.40 g of N,N-dimethylethylene-diamine (0.05 mol) dissolved in 100 mL ethanol, 10.0 g (0.1 mol) of formaldehyde (37% solution) was added. The mixture was stirred for 2 h and 23.2 g (0.1 mol) of 4-hydroxybenzenesulfonate was added. The mixture was refluxed for 12 h and allowed to cool to room temperature. Throughout the synthesis, the reaction vessel was covered with aluminum foil to prevent exposure to light. A white precipitate was isolated, washed in ethanol, and dried under vacuum. The precipitate is soluble in water. ^{1}H (500 MHz, D_2O, 25 °C): δ(ppm) 2.24 (s, 6H, methyl), 2.74 (s, 4H, ethylenic bridge), 3.78 (s, 4H, benzylic pendant arm), 6.76 (d, 2H, aromatic) 7.58 (m, 4H, aromatic protons ortho to the sulfonate). ^{13}C (500 MHz, D_2O, 25 °C): δ(ppm), 33.1 (methylic carbons), 44 (C–N ethylenic bridge), 49.3 (N–C benzylic pendant arm), 113.55, 120.4, 124.9, 128.4, 133.9, 162.5 (aromatic carbons).

2.2.3. Synthesis of L_D. To 4.40 g (0.05 mol) of N,N-dimethylethylene-diamine in 100 mL ethanol, 10.0 g (0.1 mol) of formaldehyde (37% solution) was added. The mixture was stirred for 2 h and 25.4 g (0.1 mol) of 5-sulfosalicylic acid dihydrate was added to the solution.

The mixture was refluxed for 12 h and allowed to cool to room temperature. Throughout the synthesis, the reaction vessel was covered with aluminum foil to prevent exposure to light. A white precipitate was isolated, washed in ethanol, and dried under vacuum. The precipitate is soluble in water. ^1H (500 MHz, D_2O, 25 °C): δ(ppm) 2.24 (s, 6H, methylic protons), 2.74 (s, 4H, ethylenic bridge), 3.40 (s, 4H, benzylic pendant arm), 7.04 (d, 2H, aromatic), 7.86 (d, 2H, aromatic). ^{13}C (500 MHz, D_2O, 25 °C): δ(ppm) 33.3 (methylic carbons), 44.2 (C–N ethylenic bridge), 48.2 (N–C benzylic pendant arm), 113.4, 117.7, 128.4, 132.4, 133.9, 162.2 (aromatic carbons), 171.6 (C–OOH).

3. Results and discussion

3.1. *Characterization of the interaction of L_B with the uranyl cation*

First, the spectrum of UO_2L_B was measured. The spectra (figure 1) indicate that though UO_2L_B is formed, it has no typical absorption band in the visible or near UV. This result was surprising as one expects that the band due to charge transfer from the phenolate to the uranyl should be observed, and therefore, L_B is not useful for the analytical determination of UO_2^{2+}.

3.2. *Characterization of the interaction with monodentate phenolate ligands*

In order to clarify the reason for this observation and to suggest alternative ligands for the analytical determination of trace uranyl concentrations, it was decided to measure the spectra and composition of complexes with four monodentate phenolate ligands: 3-hydroxybenzoate, resorcinol, 4-hydroxybenzenesulfonate, and salicylamide. All these ligands have a phenolate and another substituent to increase solubility in water. First, spectra of solutions containing 0.01 M UO_2^{2+} and 0.011 M of the ligands at pH 5.5 were measured. The results indicated that even at these concentrations, the complex with 3-hydroxybenzoate has no significant absorption in the visible and near UV range. The other three ligands form red-brown complexes with uranyl, and therefore, solutions containing 0.01 M UO_2^{2+} and

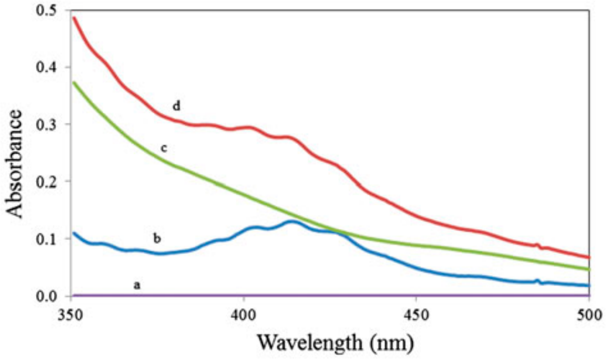


Figure 1. Characteristic absorption spectra of UO_2^{2+}, L_B, and UO_2L_B. (a) 0.2 M L_B water as a blank; (b) 0.01 M UO_2^{2+} water as a blank; (c) 0.01 M UO_2^{2+}, 0.2 M L_B, 0.01 M UO_2^{2+} as a blank; (d) 0.01 M UO_2^{2+}, 0.2 M L_B water as a blank.

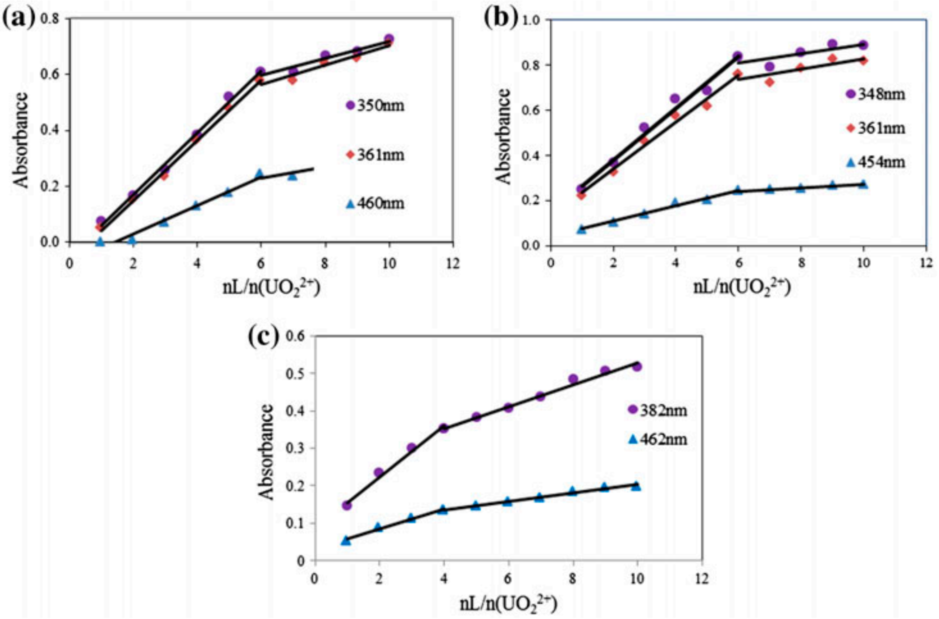


Figure 2. Dependence of the absorption on L_i/uranyl mole ratio. (a) uranyl-resorcinol; (b) uranyl-4-hydroxybenzenesulfonate; (c) uranyl-salicylamide.

0.01–0.10 M of the ligands at pH 5.5 were prepared and the dependence of the absorption of UO_2^{2+} complexes formed on the L_i concentration, at typical wavelengths, was measured. The results are summarized in figure 2. The results presented in figure 2 clearly point out that:

(1) All three ligands form complexes with uranyl. The stoichiometry of these complexes is ~1 : 6 for resorcinol and 4-hydroxybenzenesulfonate and ~1 : 4 for salicylamide.
(2) The stability constants for the complexes with 4-hydroxybenzenesulfonate are the largest as can be deduced from the slopes in figure 2 after the required concentration of the ligands was achieved.
(3) The absorption coefficient of the complex with 4-hydroxybenzenesulfonate is the highest.

3.3. *Characterization of the interaction of L_C with the uranyl cation*

Thus, it was decided to synthesize L_C and examine whether it has the desired properties. The spectra in figure 3, pH 5.5, clearly demonstrate that the complex of UO_2^{2+} with L_C has a considerable absorption in the visible region. It should be noted that the orange-red color develops immediately upon mixing. The results presented in figure 4 clearly point out that the stoichiometry of the complex is UO_2^{2+}: $L_C = 1$; therefore, the complex is probably $UO_2L_C^{2-}$. It is of interest to note that in parallel to this study, the analogous ligand N,N′-bis (5-sulfonatosalicylidene)-diaminoethane was reported to be a good extractant of uranyl

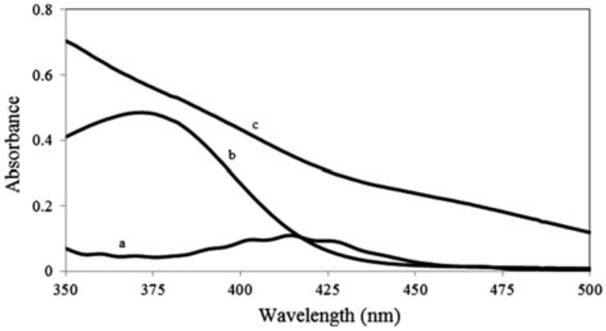


Figure 3. Characteristic absorption spectra of UO_2^{2+}, L_C, and $UO_2L_C^{2-}$. (a) 0.01 M UO_2^{2+}; (b) 0.01 M L_C; (c) 3.125×10^{-4} M UO_2^{2+}, 6.25×10^{-4} M L_C.

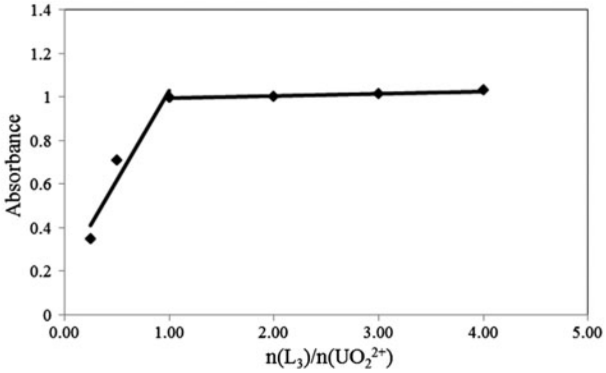


Figure 4. Stoichiometry of uranyl-L_C complex. (1×10^{-3} M UO_2^{2+}, 2×10^{-4}–4×10^{-3} M L_C, pH 5.5. The spectra were taken an hour after preparation at wavelength of 460 nm).

[13]. The sharp break of the two straight lines (figure 4) indicates that the complex has a relatively high stability constant. Therefore, it seemed of interest to check the suitability of L_C as a reagent for the analytical determination of UO_2^{2+} in dilute aqueous solutions.

3.4. *L_C as spectrophotometric reagent for the uranyl cation*

A series of solutions containing increasing concentrations of uranyl ion with excess of L_C, $[L_C] = 20[UO_2^{2+}]$, were prepared (triplicates) at pH 5.5. The absorptions of the solutions at 460 nm were measured against a blank (solvent) solution. The data of these calibration experiments and the mean and standard deviation values are presented in table S1 (see online supplemental material at http://dx.doi.org/10.1080/00958972.2015.1043287). A plot of these data shows that a linear correlation is obtained (figure 5). A molar absorption coefficient of $\varepsilon = (1.62 \pm 0.05) \times 10^3$ M^{-1} cm^{-1} is derived.

From the data presented in figure 5, one can estimate a lower limit for the apparent stability constant $K_{app} = [UO_2L_C^{2-}]/[UO_2^{2+}][L_C^{2-}]$ at pH 5.5. The results clearly point out that even at the lowest concentration studied $K_{app}[L_C^{2-}] = [UO_2L_C^{2-}]/[UO_2^{2+}] > 10$. As $1.0 \times 10^{-3} > [L_C^{2-}] > 9.5 \times 10^{-4}$ M one obtains $K_{app} > 1.1 \times 10^4$ M^{-1} at this pH.

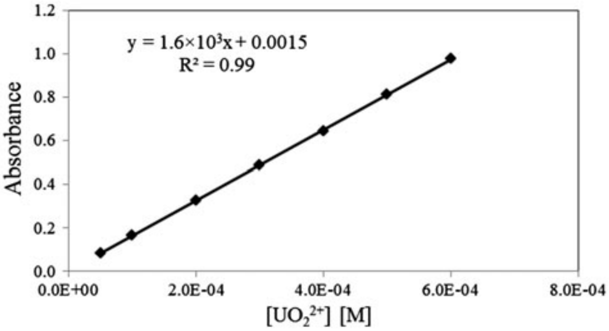


Figure 5. Molar absorption coefficient for the uranyl-L_C (measured at 460 nm, pH 5.5, $[L_C]/[UO_2^{2+}] = 20$).

A reagent useful for quantitative analysis of UO_2^{2+} has to have a significantly different spectrum than that of the complexes of other transition-metal cations, and the ligand has to be present in a large excess over all the relevant cations present in the solution. $Co(H_2O)_6^{2+}$ and $Ni(H_2O)_6^{2+}$ were chosen as representative cations (It should be noted that M_{aq}^{III} cations, M transition metal, are not soluble at pH 5.5). The spectra of solutions containing 2.0×10^{-3} M L_C^{2-} and 1.0×10^{-4} M of one of the following cations: UO_2^{2+}, Co^{2+}, and Ni^{2+} are presented in figure 6. The spectra of the complexes of Co(II) or Ni(II) have no significant absorption bands at $\lambda > 460$ nm. This observation is in accord with expectations for LMCT transitions, as UO_2^{2+} is a considerably stronger oxidant than $Co(H_2O)_6^{2+}$ and $Ni(H_2O)_6^{2+}$.

Comparison of L_C to other spectrophotometric reagents that have been suggested for the analysis of the uranyl ion in aqueous and organic solutions; AzIII [14–16], "isoamethryn [17], 4-(2-pyridylazo)resorcinol(PAR) [18, 19], 1-(2-pyridylazo)-2-naphthol (PAN) [20], 2-(5-bromo-2-pyridylzo)-5-diethylaminophenol (bromo-PADAP) [21], and p-carboxychloro-phosnazo (CPApk) [22] indicate that all these reagents are considerably more sensitive than the proposed ligand and enable detection limits of several μM, in a 1 cm cell". For example, the CPApk reagent, reacting with uranyl in acidic medium, is very sensitive. The addition of

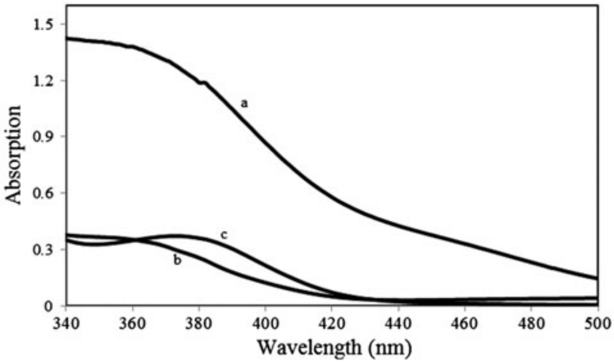


Figure 6. Spectra of the complexes of UO_2^{2+}, Ni^{2+}, and Co^{2+} with L_C^{2-}; (a–c) 2.0×10^{-3} M L_C^{2-} pH 5.5 and (a) 1.0×10^{-4} M of UO_2^{2+}, (b) 1.0×10^{-4} M Co^{2+}, (c) 1.0×10^{-4} M Ni^{2+}.

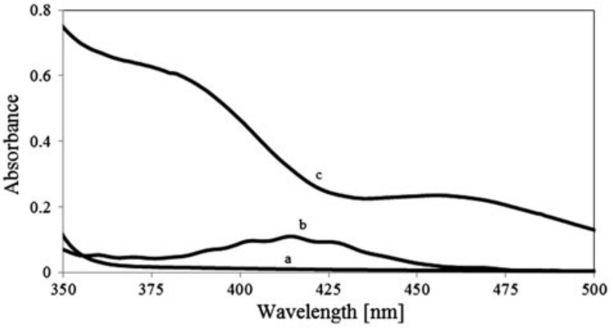


Figure 7. Characteristic absorption spectra of UO_2^{2+}, L_D^{2-}, and $UO_2L_D^{2-}$. (a) 0.01 M L_D^2, (b) 0.01 M UO_2^{2+}, (c) 2.5×10^{-3} M UO_2^{2+}, 2.5×10^{-3} M L_D^{2-}.

the surfactant polyvinyl alcohol increases both the sensitivity and the stability of the uranyl complex thus formed with molar absorptivity of 2.72×10^5 M^{-1} cm^{-1}. However, the designed ligand, L_C^{2-}, has some advantages: It is water soluble and thus is suitable for aqueous solution analysis with no need of an extraction stage in the procedure, as opposed to PAN; and 4-(2-pyridylazo)resorcinol, 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol has a typical absorption at 578 nm, but the complexation reaction demands 40 min, while our reagent complexes immediately. The currently used reagent Arsenazo-III has a deep purple color and as such is not appropriate for colorimetric analyses. The ligand presented by Albo *et al.* [12] has very similar properties, but is water insoluble due to the two tert-butyl substituents.

3.5. *Characterization of the interaction of L_D with the uranyl cation*

Finally, it was decided to study the source of the differences between L_B and L_C as ligands for uranyl. For this purpose, the ligand L_D was synthesized. The spectrum of the complex $UO_2L_D^{2-}$ is presented in figure 7. A comparison of the spectra presented in figures 3 and 7 indicates that though the spectra are similar, the absorption coefficients of $UO_2L_D^{2-}$ are considerably smaller than those of $UO_2L_C^{2-}$. The results presented in figure S1 point out that the stoichiometry of the complex is $[UO_2^{2+}]/[L_D^{2-}] = 1$ and that the complex has a high stability constant. From figure S2, one obtains $\varepsilon(UO_2L_D^{2-})_{455} = 93$ M^{-1} cm^{-1}, i.e. ca. 17 times smaller than that of $UO_2L_C^{2-}$. It is tempting to speculate that the carboxylates, which are relatively strong bases, are, at pH 5.5, better ligands than the phenolates, due to the higher pK_a of the latter. The LMCT bands of carboxylates are expected to be shifted considerably to the UV in comparison with the phenolates thus explaining the results. However, obviously the intensity and absorption wavelength of a LMCT band are strongly dependent on the coordination mode, geometry and the identity of the coordinating ligand function involved in the M–L bond. Following this assumption, in $UO_2L_D^{2-}$ less than 10% of the complex possesses a ligand bonding situation similar to $UO_2L_C^{2-}$.

4. Conclusion

L_B, L_C, and L_D form water soluble complexes with the uranyl cation. The results obtained for the ligands L_B and L_D that contain both phenolate and carboxylate substituents indicate that the carboxylates compete with phenolate groups as ligands for the central uranyl cation, resulting in blue shifting of the absorption bands of the complexes. Thus, these ligands are not suitable to be used as spectrophotometric reagents for uranyl.

As opposed to the former ligands the reaction of L_C with uranyl is accompanied by an immediate deep color change with typical absorption at 450–500 nm with relatively high molar absorption coefficients. The results indicate that this easily synthesized ligand can be used as a reagent for the analysis of the uranyl concentration in aqueous solutions or as a colorimetric sensor for determining the presence of uranyl ions in solutions.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This study was supported by a joint grant between the JRC and NRCN for which I.Z. and D.M. are most grateful.

References

[1] M.N. Abbas, A.M. Homoda, G.A.E. Mostafa. *Anal. Chim. Acta*, **436**, 223 (2001).
[2] H.G. Brittain. *Anal. Lett.*, **10**, 263 (1977).
[3] Y. Hirano, Y. Ogawa, K. Oguma. *Anal. Sci.*, **19**, 303 (2003).
[4] L. Jancar, B. Slezackova, L. Sommer. *Talanta*, **36**, 549 (1989).
[5] S. Joannon, P. Telouk, C. Pin. *Spectrochim. Acta, Part B: At. Spectrosc.*, **52**, 1783 (1997).
[6] G. Kwapulinska, B. Janoszka. *Fresenius', J. Anal. Chem.*, **338**, 641 (1990).
[7] J.A. Liyanage, D.M. Taylor, D.R. Williams. *Anal. Proc. Incl. Anal. Commun.*, **32**, 217 (1995).
[8] M. Raileanu, G. Grigoriu. *J. Radioanal. Nucl. Chem.*, **292**, 493 (2012).
[9] A. Suresh, D.K. Patre, T.G. Srinivasan, P.R.V. Rao. *Spectrochim. Acta, Part A: Mol. Biomol. Spectrosc.*, **58**, 341 (2002).
[10] L.S.G. Teixeira, A.C.S. Costa, S.L.C. Ferreira, M.L. Freitas, M.S. Carvalho. *J. Braz. Chem. Soc.*, **10**, 519 (1999).
[11] H.B. Ulusoy. *J. Radioanal. Nucl. Chem.*, **302**, 497 (2014).
[12] Y. Albo, M. Saphier, E. Maimon, I. Zilbermann, D. Meyerstein. *Coord. Chem. Rev.*, **253**, 2049 (2009).
[13] C.A. Hawkins, C.G. Bustillos, R. Copping, B.L. Scott, I. May, M. Nilsson. *Chem. Commun.*, **50**, 8670 (2014).
[14] G.E. Collins, Q. Lu. *Anal. Chim. Acta*, **436**, 181 (2001).
[15] M. Khan, S. Bukhari, A. Ali, K. Liaqat, S. Fazal. *J. Radioanal. Nucl. Chem.*, **289**, 113 (2011).
[16] H. Rohwer, N. Rheeder, E. Hosten. *Anal. Chim. Acta*, **341**, 263 (1997).
[17] J.L. Sessler, P.J. Melfi, D. Seidel, A.E.V. Gorden, D.K. Ford, P.D. Palmer, C.D. Tait. *Tetrahedron*, **60**, 11089 (2004).
[18] T.M. Florence, Y. Farrar. *Anal. Chem.*, **35**, 1613 (1963).
[19] L. Sommer, V.M. Ivanov, H. Novotná. *Talanta*, **14**, 329 (1967).
[20] S. Shibata. *Anal. Chim. Acta*, **22**, 479 (1960).
[21] D.A. Johnson, T.M. Florence. *Anal. Chim. Acta*, **53**, 73 (1971).
[22] Y. Ru, L. Yan, S. Guilan, W. Tao, P. Jiaomai. *Anal. Chim. Acta*, **314**, 95 (1995).