

STUDY OF THE UO_2^{2+} –ACID-2-AMINO-1-NAPHTALEN SULPHONIC (ANS) SYSTEM IN SOLUTION

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In the present paper a new chelating agent for the extraction of the uranyl ions from the acid solution, the 2-amino-1-naphthalene sulphonic acid, was introduced. The complex was synthesized in solution, the ratio of M/L combination, which is 1/2, being also determined. IR and UV-VIS spectrometry techniques were used to analyze the complex. The PM3 semiempirical methods were used for the theoretical study of the ligand and complex structures. Also the symmetry of the structures was investigated.

INTRODUCTION

Actinides' capacity of forming complex combinations depends on both the ion's charge and size, and on the ligand's type. The shorter the metallic ion's radius, the higher the complexation probability. Metallic ion's charge has a reverse influence in the case of uranium. Actinides' ions are included in the class of Lewis acids of the “a” type – known as preferring especially O-donor and N-donor ligands for coordination.¹

The most common uranium compounds are those containing the linear, symmetrical UO_2^{2+} ion. This ion readily adds 4-6 donor atoms in its equatorial plane.²⁻⁵

The investigation of the complex compounds formed by the uranyl ions is very interesting because these compounds are used in the extraction processes of uranyl ions from aqueous solutions obtained in the different technologies of uranium processing. Some of these compounds were obtained using oxygen donor ligand as well as many nitrogen donors and even sulfur donors.

During the research for new chelating agents for the extraction of metal ions from acid solution, the 2-amino-1-naphthalene sulphonic acid (ANS) was introduced. The present study is devoted to the formation of a complex combination between the uranyl ions (employed as complex generators) and the ANS – applied as a ligand.

In parallel with experimental results, theoretical investigations of structures (ligand and complex) using the PM3 semiempirical method were performed.^{6,7}

RESULTS AND DISCUSSION

The composition of the formed complex was determined by the method of the molar ratio, Job's method,⁸ using a CECIL spectrophotometer at 210 nm wavelength. Thus, a fixed volume from the uranyl solution and different volumes of ligand solution were considered for the study. The results obtained are listed in Table 1.

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Table 1
Data on the composition of the UO_2^{2+} – ANS complex obtained from Job's method

$V_{\text{UO}_2^{2+}}$, mL	1	1	1	1	1	1	1	1	1	1	1	1
V_{ANS} , mL	0.5	0.8	1.1	1.4	1.7	2.0	2.3	2.6	2.9	3.2	3.5	3.8
$V_{\text{H}_2\text{O}}$, mL	4.5	4.2	3.9	3.6	3.3	3.0	2.7	2.4	2.1	1.8	1.5	1.2
$\frac{[\text{L}]}{[\text{M}]}$	0.5	0.8	1.1	1.4	1.7	2.0	2.3	2.6	2.9	3.2	3.5	3.8
Abs.	0.216	0.272	0.324	0.375	0.434	0.491	0.541	0.570	0.595	0.612	0.624	0.631

Application of the polynomial regression method⁹ for the determination of the law operating for the parameters given in Table 1, of the $y = ax^2 + bx + c$ type, with variables: $y = \text{Abs}$, $x = [\text{L}]/[\text{M}]$, did not lead to significant results for the system considered. Consequently, data processing was resumed considering grouping of the experimental coordination points in pairs. Thus, a row of straight lines with different slopes is obtained; for any two concurrent (*i.e.*, possessing a common point, k) straight lines, the calculated slopes are compared with the relation:

$$m = \frac{y_2 - y_1}{x_2 - x_1} \quad (1)$$

where indices 1 and 2 represent the points determining the straight line under discussion. In this way, the data listed in Table 2 are obtained.

Table 2
Values of the straight line's slopes obtained from the experimental data

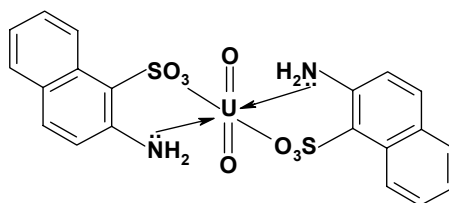
Line	1-2	2-3	3-4	4-5	5-6	6-7	7-8	8-9	9-10	10-11	11-12
Slopes	0.186	0.173	0.170	0.196	0.190	0.166	0.096	0.083	0.056	0.040	0.023

The slope differences, $|\Delta m|$, around a given point were calculated starting from the second experimental point. The point in which the highest value of this difference will be recorded is undoubtedly the point corresponding to the L/M combination ratio looked for, as it corresponds to the most accentuated slope change along the whole experimental line under study. The differences obtained using the relation $|\Delta m|_k = |m_{k,k+1} - m_{k-1,k}|$, ($k=2-11$) where k represents the experimental point under discussion, are given in Table 3.

Table 3
Differences of the calculated slopes

Point considered	2	3	4	5	6	7	8	9	10	11
$ \Delta m $	0.013	0.003	0.026	0.006	0.024	0.070	0.013	0.027	0.016	0.017

Consequently, the largest slope difference occurs in the case of point $k = 7$, which corresponds to an L/M combination ratio of 2.3/1 approximately 2/1. In this case the formula proposed by the authors of the present study for such a combination ratio is $[\text{UO}_2(\text{ANS})_2]$, the structure of which is:



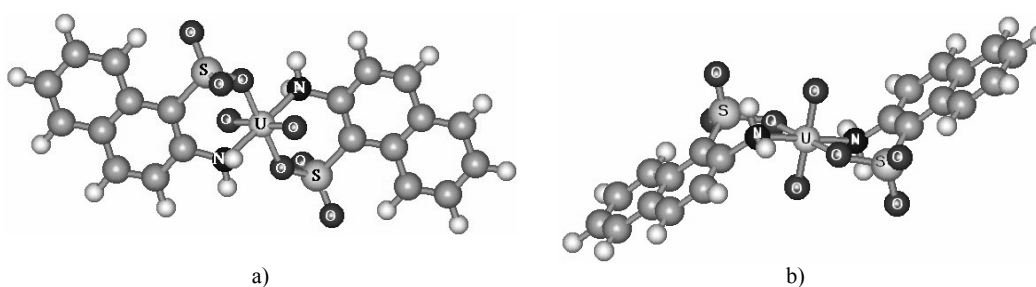
The data from the elemental analysis are reported in Table 4. The uranyl ions were determined spectrophotometrically with Arsenazo III.

Table 4

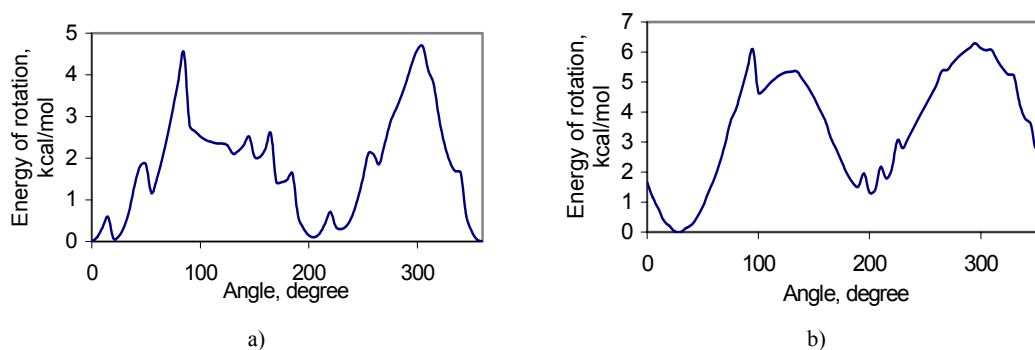
Theoretical and experimental results of the elemental analysis

H, %		C, %		N, %		S, %		U, %	
theor.	exp.	theor.	exp.	theor.	exp.	theor.	exp.	theor.	exp.
2.346	2.25	35.19	35.094	4.10	4.00	9.38	9.28	34.89	34.794

The structure of the ligand and of the complex obtained was simulated with the HyperChem programs,¹⁰ while structures' optimization was made by the PM3 semi-empirical method,^{6,7} with the Polak-Ribiere algorithm¹¹ and the condition of convergence RMS gradient of 0.001 kcal/(Å·mol). Optimization of the complex's spatial structure shows that this is a molecular structure with a reduced symmetry degree, more exactly, belonging to the symmetry group C₁ – as shown in Fig. 1.

Fig. 1 – Proposed spatial structure for the [UO₂(ANS)₂] complex – in the xy plane (a) and, respectively, xz plane (b).

For the establishment of the ligand's structure, ANS, characterized by the lowest value of the formation energy, the –SO₃H and –NH₂ groups were rotated, while the variation of the rotation energy obtained in the two cases is plotted in Fig. 2. One may observe that, the rotation barrier of the sulphonic group is of about 5 kcal/mol and, in the case of the amino group, of about 6 kcal/mol.

Fig. 2 – Relative variation of the energy of ligand's formation during rotation of group SO₃H (a) and NH₂ (b).

Atoms' numbering and the structure of the most stable conformer for the ligand molecule are represented graphically – from an energetic viewpoint – in Fig. 3.

Some theoretical values of the parameters characteristic for the ligand's structure are listed in Table 5.

Optimization of the ligand's structure evidences the fact that this may have an intramolecular hydrogen bond between the –NH₂ and –SO₃H groups, between a H atom from the –NH₂ group and an O atom from the –SO₃H substituent, or between the H atom from the sulphonic group and the non-involved electrons of the N atom from the amino group.¹² In the ligand's most stable structure, the distance between a H(21) atom of the –NH₂ group and an O(20) atom of the –SO₃H one is of 1.81 Å.

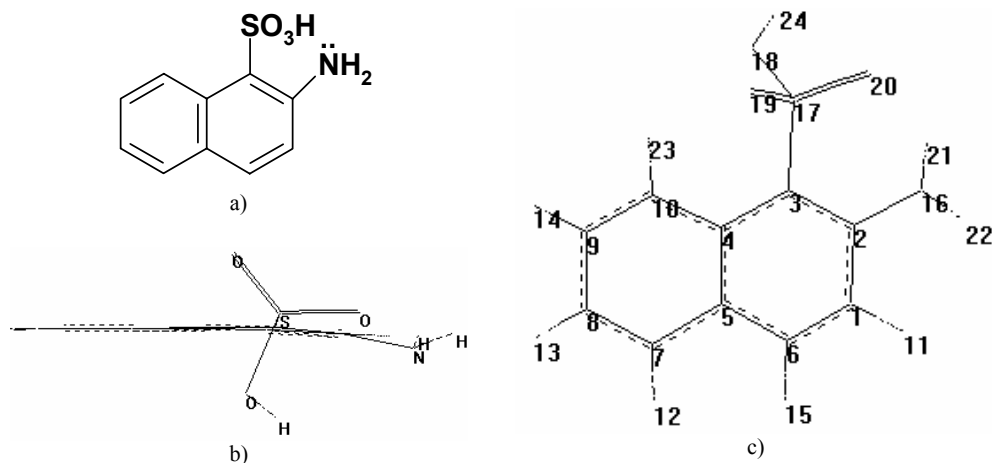


Fig. 3 – Formula (a), spatial structure (b) and numbering of atoms (c) for the most stable conformation of the ANS.

Table 5

Some geometrical values characterizing ligand's energetically most stable structure

Distance, Å		Angle, degree		Dihedral angle, degree	
3-17	1.76	3-17-20	109.92	2-3-17-20	-0.95
17-20	1.47	3-12-19	114.10	2-3-17-19	134.05
17-19	1.43	3-17-18	102.62	2-3-17-18	-111.12
17-18	1.68	17-18-24	115.75	3-17-18-24	124.1
18-24	0.95	18-17-20	104.00	3-2-16-21	-20.73
2-16	1.41	18-17-19	106.56	3-2-16-22	-155.55
16-21	1.01	19-17-20	117.88	16-2-3-17	15.20
16-22	0.99	2-3-17	121.58	16-21-20-17	-0.18
20-21	1.81	2-16-22	113.94		
		2-16-21	115.40		
		21-16-22	114.08		
		3-2-16	122.75		

One may observe from Table 5 that the lengths of 16-21 and 17-20 atoms' bonds are slightly higher than those of the 16-22 and, respectively, 17-19 ones, which is indicative of the possible existence of a hydrogen bridge between atoms 21 and 20. Thus, the formation of a new cycle of six atoms is possible.

Atom's charge density for the ANS structure is represented in Fig. 4, which also evidences that the difference of charge density between atoms 21 and 22 is higher than that corresponding to the similar atoms 22 and 19 – a new argument supporting the hypothesis of a hydrogen bond creation between the corresponding atoms.

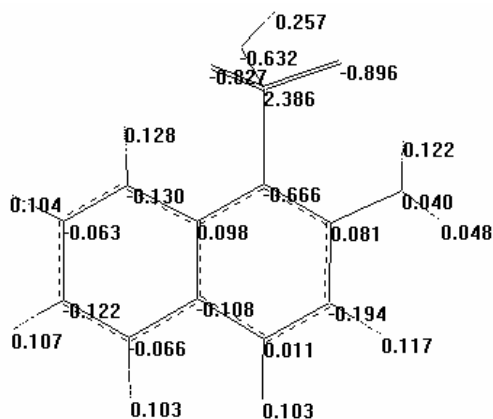


Fig. 4 – Density of atoms' charge corresponding to the ligand's most stable energetic structure.

Optimization of the complex's structure shows that this is not planar, having instead a chair-like shape (Fig. 1b). Orientation of the NH₂ group corresponds to a tetrahedral structure of the nitrogen atom, which involves its pair of non-participating electrons in the coordinative bond with the uranium atom.

Analysis of the UV-VIS spectra for the complex and ligand structure (Fig. 5) puts into evidence the occurrence of multiple bands that may be attributed as follows:¹

- transitions permitted by the selection rules of the $5f^n \rightarrow 5f^{n-1}6d^1$ type, which leads to bands characterized by high values of the molar extinction coefficient, ϵ , exceeding 1,000 L/mol·cm, at $\lambda = 240$ nm in the complex under study; the absorbance decreases because the ligand is employed in the coordination to uranyl ions;

- charge transfer bands, determined by an electron's transition from one ligand's orbital in the 5f level of the metallic ion;

- intra-ligand bands (ligand's own ones), $\lambda = 343$ nm, corresponding to an $n \rightarrow \pi^*$ transition. This band is slightly shifted in the complex at $\lambda = 340$ nm, with a significant reduction of the molar extinction coefficient (from $\epsilon = 33018$ L/mol·cm at $\epsilon = 698$ L/mol·cm) in the complex spectrum because the non-participating electrons of the amino group are employed in the coordination of the uranyl ions.

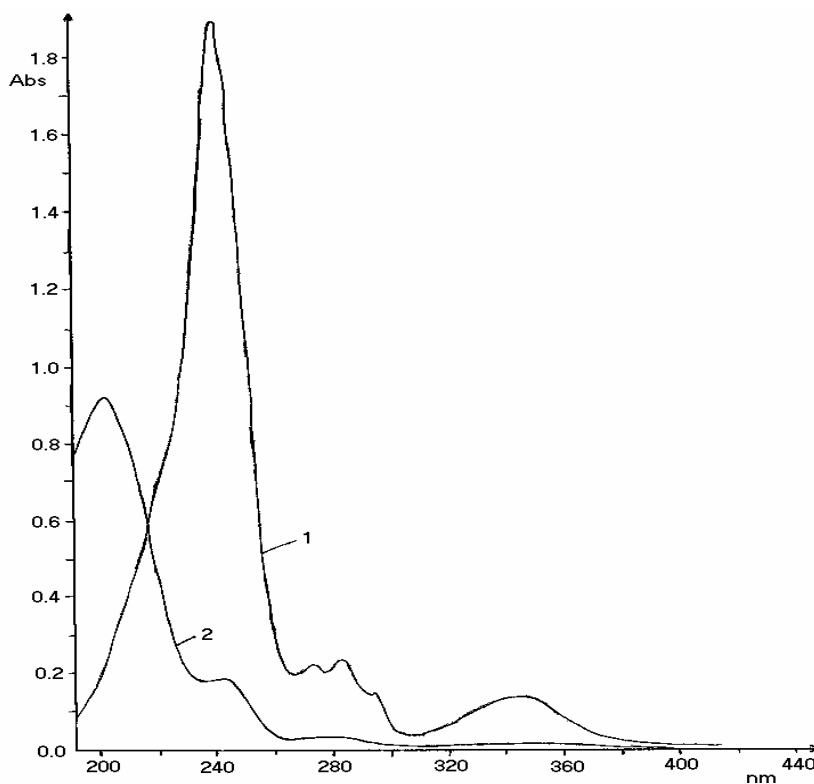


Fig. 5 – UV-VIS spectrum for ANS (1) and UO₂²⁺-ANS (2).

Theoretical ligand's and complex's electronic spectra, obtained with the HyperChem package program, were based on the orbital criterium, on considering the last three occupied energetic levels and the first three free ones. As to ligand's structure, it was evidenced that the first transition permitted $n \rightarrow \pi^*$, is situated at 344.13 nm, while transition $\pi \rightarrow \pi^*$ occurs at 260.14 nm. As to the simulation of the complex's electronic spectrum, one may observe that the first transition permitted occurs at 267.6 nm, which would correspond to a $\pi \rightarrow \pi^*$ transition. Disappearance, in the complex's spectrum, of the band from 344.13 nm in the ligand's spectrum, corresponding to an $n \rightarrow \pi^*$ type transition, indicates the fact that the non-participating electrons of the amino group are employed in the formation of a dative bond with the central atom.

On analyzing the ligand's and the complex's IR spectrum (Fig. 6), one may observe the occurrence of a band at about 1500 cm⁻¹, which may be attributed to the $\delta_{(\text{NH}_2)}$ vibrations in ANS, superposed – in the

complex – with cycles' vibration. At the same time, another band appears around 3450 cm^{-1} , as a result of $\nu_{(\text{NH}_2)}$ type vibrations.^{2,4} The band occurring at 888.059 cm^{-1} may be attributed to $\nu_{\text{as}}(\text{O-U-O})$, while that from 826.348 cm^{-1} is attributable to $\nu_{\text{sim}}(\text{O-U-O})$ vibrations³⁻⁵, which confirms the presence of UO_2^{2+} in this complex. The band attributed to the $\nu_{\text{C-S}}$ vibrations, occurring in the ligand at about 700 cm^{-1} , is strongly diminished in the complex, probably as a result of the involvement of an oxygen atom, linked to the sulphur atom, in the coordination at the metallic atom.

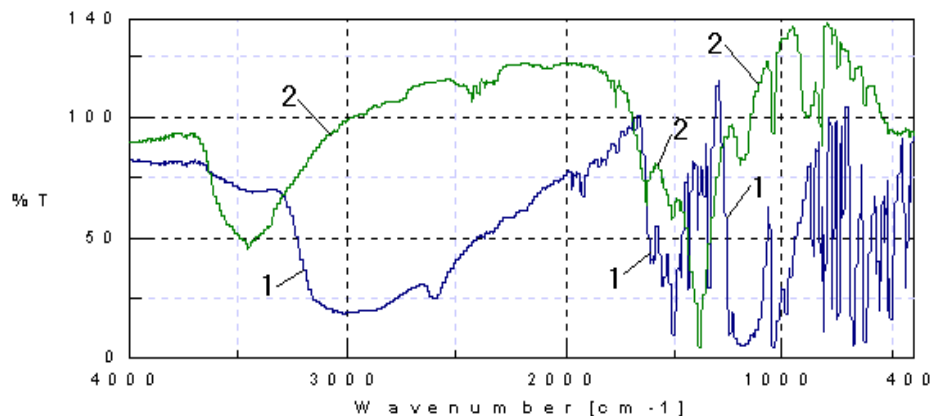


Fig. 6 – IR spectra for ANS(1) and for UO_2^{2+} -ANS (2).

Simulation of the ligand's vibration spectrum evidences the following aspects: the symmetrical valence vibration of the N-H links from the NH_2 group was determined at 3324 cm^{-1} , while the asymmetrical vibration of the same links – at 3498 cm^{-1} ; the vibration of the OH link from the SO_3H group was determined at 3897 cm^{-1} .

Simulation of the complex's vibration spectra evidences the existence of two, doubly-generated vibrations, which correspond to the vibrations of the N-H links from the NH_2 group – symmetrical at 3317 cm^{-1} and asymmetrical at 3442 cm^{-1} .¹³ Shifting of the vibration frequencies of the NH_2 group demonstrates once more the involvement of this group in the creation of a link with the central metallic atom. At the same time, this group's vibrations may be affected, too, by the existence of a hydrogen link that may be formed, within the complex, between the hydrogen atom of the amino group and an oxygen atom from the SO_3H group.

All such calculations and simulations of the ligand's and complex's structure, along with the IR and UV-VIS spectra, represent arguments supporting the formation of a complex between ANS and UO_2^{2+} , possessing the structure and characteristics discussed in the present study.

EXPERIMENTAL

Hexahydrated uranyl nitrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was utilized as a source of uranyl ions, while the applied ligand – ANS was employed as such, without any additional processing.

ANS solutions were prepared in weakly alkalized water ($\text{pH} \approx 8$), and uranyl nitrate solutions in deionized water, both in $1 \cdot 10^{-2}\text{ M}$ concentration.

The complex, obtained in normal laboratory conditions, through successive recrystallizations, appears as a yellow-orange powder. Spectral investigations on the structure of the complex obtained were developed on a JASCO FT-IR 660 plus spectrophotometer (KBr pellets) – for the vibration spectrum's recording, as well as on a CINTRA spectrophotometer, for the UV-VIS spectrum.

CONCLUSIONS

A new complex of uranyl was synthesized, using ANS as ligand. Spectral analysis confirmed the formation of the complex combination. The composition of the complex was determined, the combination ratio found being $M/L = 1/2$. The spatial structure proposed for the obtained complex was considered as belonging to a symmetry group. Calculations were made for the structure's simulation and determination of

both ligand's and complex's vibration and electronic spectra, values in agreement with the experimental data being thus obtained.

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