

URANYL NITRATE COMPLEX WITH THE LIGAND 1,3-DITHIANE-1-OXIDE (DTSO)

Pedro Miranda Jr.^{1,2}, Marcelo F. Máduar¹, Maria Claudia F.C. Felinto¹, Duclerc F. Parra¹ and Hermi Felinto³

¹Instituto de Pesquisas Energéticas e Nucleares - IPEN-CNEN/SP

Av. Prof. Lineu Prestes 2.242

05508-900, Butantã, São Paulo, SP, Brasil

²Faculdades Oswaldo Cruz – FOC

Rua Brigadeiro Galvão, 540

01151-000, Barra Funda, São Paulo, SP, Brasil

³Instituto de Química, Universidade de São Paulo - USP

Av. Prof. Lineu Prestes

05508-970 Butantã, São Paulo, SP, Brasil

ABSTRACT

Uranyl nitrate complex with 1,3-dithiane-1-oxide (DTSO) was synthesized by reaction of the hydrated uranyl nitrate with DTSO in ethanol solution. The complex was characterized by CHN microanalytical and infrared spectra. The emission spectrum of the uranyl ion shows four groups of lines of intrinsic luminescence of the matrix. Thermal behavior of the complex was investigated by thermogravimetric (TG) and differential scanning calorimetric (DSC) analysis. The structure of the complex resolved by X-ray showed that the uranium atom is octa-coordinated with two oxygen atoms, two bidentate nitrate ions and two DTSO ligands.

Keywords: uranyl nitrate, 1,3-dithiane-1-oxide, structure, thermal analysis, luminescence

I. INTRODUCTION

The uranyl ion possesses some properties which make it a potential component for a solar energy conversion system. It absorbs light in the shorter-wavelength range of solar spectrum, producing a relatively long-lived excited state[1]

Uranyl ion luminescence is often studied in non-complexing, acidic solutions where it exists entirely in the simple hydrated form $(\text{UO}_2^{2+})_{\text{aq}}$ or else in complexing media such as phosphoric acid, phosphate, fluoride or sulphate which enhance its luminescence for its determination, but few papers were reported in solid state.

The uranyl ion (UO_2^{2+}) has a linear structure, where the uranium(VI) is placed between two oxygen ions. The hydrated uranyl nitrate is a yellow crystal with 2, 3 or 6 water molecules. This salt has the structure $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot x\text{H}_2\text{O}$ where $x = 0, 1$ and 4 . The uranium is octa-coordinated in which the linear uranyl ion is coordinated to two water molecules and two bidentate nitrate ions. Other water molecules are linked by hydrogen bonding [2]. The early property of this salt is the high solubility in many organic solvents, permitting the solvent extraction of uranium from aqueous solutions [3]. Among the uranyl applications, it can be cited its use as actinometers, solar collectors and photocalyst [4,5,6].

The use of sulfoxides as neutral ligands in lanthanide complexes has been an object of investigation. Complexes containing dithiane sulfoxides have been prepared, with the following compositions: $\text{Ln}(\text{pic})_3 \cdot 3\text{DTSO}$ (pic = picrate, DTSO = 1,3-dithiane-1-oxide) [7], $\text{Ln}(\text{pic})_3 \cdot 4\text{-cis-DTSO}_2 \cdot 2\text{H}_2\text{O}$ (pic = picrate, cis-DTSO₂ = cis-1,3-dithiane-1,3-dioxide) [8], $\text{Ln}(\text{pic})_3 \cdot 1.5\text{TDTD}$ (pic = picrate, TDTD = trans-1,4-dithiane-1,4-dioxide) [9,10].

The purpose of this work is the study of the synthesis and characterization of an uranyl complex obtained by reaction of the ligand 1,3-dithiane-1-oxide (DTSO) with the uranyl nitrate hexahydrated and of their luminescent properties.

II. EXPERIMENTAL

The ligand 1,3-dithiane-1-oxide (DTSO), molecular formula $\text{C}_4\text{H}_8\text{S}_2\text{O}$, with the structural formula presented in Figure 1, was prepared by oxidation of 1,3-dithiane dissolved in methanol at 5°C with sodium metaperiodate in aqueous solution, as described by Carlson with some modifications [6, 11].

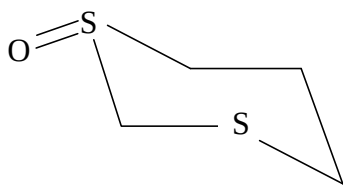


Figure 1. Structural Formula of the DTSO Ligand.

The complex was synthesized by reaction of an ethanolic solution of hydrated uranyl nitrate and the DTSO ligand in the same solvent at 50 °C (molar ratio 1:2). Yellow crystals were obtained after ten days, at room temperature. The crystals were separated, washed with cold ethanol and maintained under vacuum over anhydrous calcium chloride.

CHN microanalytical procedures were performed in a Perkin-Elmer 240 instrument. IR spectra were recorded on a Nicolet FTIR-8100 spectrometer using KBr pellets.

The structure of the uranyl complex was determined by single crystal X-ray analysis. The X-ray crystallographic data were recorded on an Enraf-Nonius CAD-4 Mach3 diffractometer in the $\omega/2\theta$ scan mode at 293 K, using graphite monochromated MoK α radiation ($\lambda=0.71073$ Å).

The excitation and emission spectra of the $[\text{UO}_2(\text{NO}_3)_2(\text{C}_4\text{H}_8\text{S}_2\text{O})_2]$ powder samples were performed in a SPEX Fluorolog-2 spectrofluorimeter, model FL212 system, double grating 0.22 m SPEX 1680 monochromators, and a pulsed lamp as excitation source using the front face mode. This apparatus was fully controlled by a DM3000F spectroscopic computer.

Thermal behavior of the complex was investigated by thermogravimetric (TGA) and differential scanning calorimetric (DSC) analysis. TG/DTG were performed in a TGA/SDTA 851 instrument under dynamic air atmosphere (50 mL min⁻¹), heating rate of 10°C min⁻¹ up to 900 °C. DSC measurements were performed in a dynamic nitrogen atmosphere (50mL min⁻¹) at heating rate of 10 °Cmin⁻¹ up to 700 °C, using a DSC-50 Shimadzu cell.

III. RESULTS AND DISCUSSION

The results of microanalyses of the complex: C (14.7%), H (2.4%) and N (4.0%) agree with the calculated: 14.4, 2.4 and 4.2%, respectively. The contents of C, H, and N are in agreement with the proposed stoichiometry $[\text{UO}_2(\text{NO}_3)_2(\text{C}_4\text{H}_8\text{S}_2\text{O})_2]$, where $\text{C}_4\text{H}_8\text{S}_2\text{O}$ is the DTSO ligand.

According to IR spectra, Figure 2, shifts of ν_{SO} of the free ligand (1049 cm⁻¹) to lower frequencies in the complex (960 cm⁻¹) indicate that the DTSO is coordinated to the uranium atom through the oxygen. The UO_2^{2+} symmetric stretching band was found at 924 cm⁻¹. Bands attributed to the nitrate ions ($\nu_1=1278\text{cm}^{-1}$, $\nu_2=1029\text{cm}^{-1}$, $\nu_3=747\text{cm}^{-1}$, $\nu_4=1524\text{cm}^{-1}$ and $\nu_6=807\text{cm}^{-1}$) suggest the bidentate coordination.

Table 1 presents the crystal data collection and refinement data. The single crystal structure, Figure 3, shows that the uranium is octa-coordinated, where the linear uranyl ion is coordinated to two monodentate DTSO ligands and two bidentate nitrate ions. The structure of the complex showed that the crystals are triclinic and space group $P\bar{1}$.

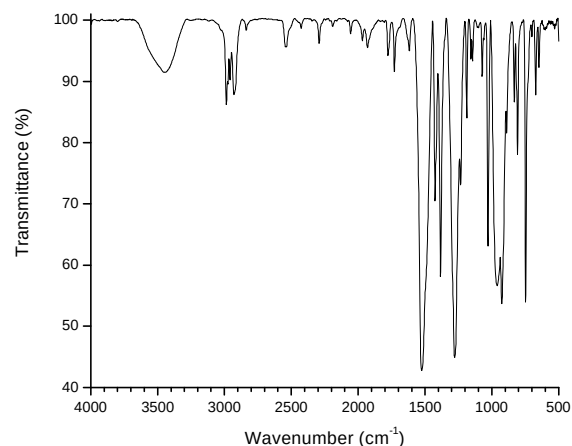


Figure 2: Infrared spectra of the complex $[\text{UO}_2(\text{NO}_3)_2(\text{C}_4\text{H}_8\text{S}_2\text{O})_2]$

TABLE 1: Crystallographic data of the structure.

Empirical formula	$\text{C}_8\text{H}_{16}\text{N}_2\text{O}_{10}\text{S}_4\text{U}$
Formula weight	666.51
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system,	triclinic
space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	5.958(1)
b (Å)	8.045(1)
c (Å)	10.240(1)
α (°)	78.42(1)
β (°)	71.43(1)
γ (°)	77.91(1)
Volume (Å ³)	490.8(1)
Molecules per cell, Z	1
Calculated density, D_c , (g cm ⁻³)	2.25

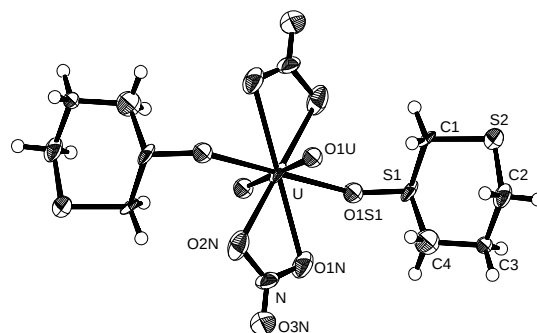


Figure 3. Structure of the complex $[\text{UO}_2(\text{NO}_3)_2(\text{C}_4\text{H}_8\text{S}_2\text{O})_2]$

The uranyl ion exhibit a highly characteristic luminescence both in solid state and in solution. The luminescence phenomenon is assigned to emission from the lowest $^3\Pi_u$ state, displaying considerable vibrational structure. As in the absorption spectrum, the shape and intensity of the emission spectrum are very sensitive to the particular environment of the UO_2^{2+} species.

Figure 4 shows the emission spectra of the complex $[\text{UO}_2(\text{NO}_3)_2(\text{C}_4\text{H}_8\text{S}_2\text{O})_2]$ at 298 K. As expected, characteristic lines in visible spectra appear with maxima in 499.5, 501.35, 515.7, 516.57, 538.50, 544.10, 564.09 and 574.68 nm when excited in 400 nm. When compared with the precursor salt (omitted spectra), loss in the luminescence intensity is observed. The excitation spectra presented in. In the figure 5 we present the excitation spectra monitored in three different wavelengths and the profile of spectra are the same in the region of 350-500nm. The intensity is slowly modified. In the region of 250 – 300nm we can see the displacement of the band attributed to the matrix to the ultraviolet region with decrease of excitation.

Comparing the spectra in two different excitation lines Figure 4 (400 and 290 nm) using the same slit, it was possible to establish that the excitation in 400 nm is more effective than in 290 nm in the sequence of absorption, energy-transfer, emission involving distinct absorbing and emitting components, while the profiles of the spectra are the same.

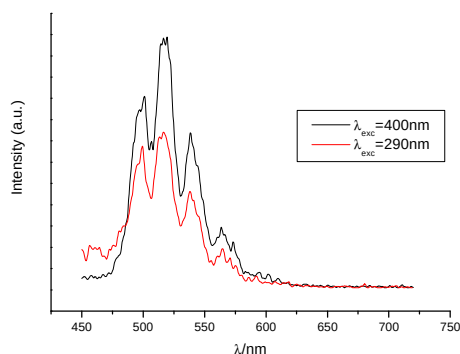


Figure 4. Emission Spectra of the Complex $[\text{UO}_2(\text{NO}_3)_2(\text{C}_4\text{H}_8\text{S}_2\text{O})_2]$ Excited in 290 and 400 nm at Room Temperature.

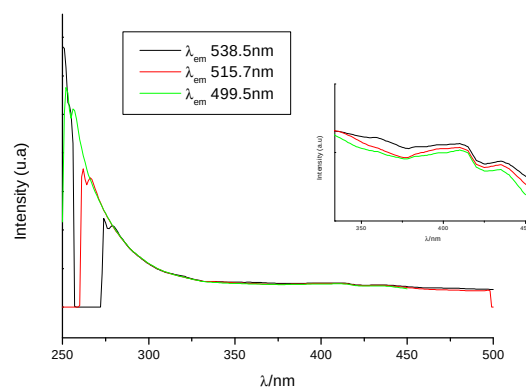


Figure 5. Excitation Spectra of the Complex $[\text{UO}_2(\text{NO}_3)_2(\text{C}_4\text{H}_8\text{S}_2\text{O})_2]$ with Emission Monitored at Room Temperature.

Figure 6 presents the results of thermal decomposition of the complex. The results obtained from TG and DTG curves and stoichiometry data suggested that the thermal decomposition, in the temperature range investigated (25 – 1200°C), occurs in four stages. The first event is the loss of one ligand occurring below 220°C, corresponding to 20.5% of mass loss with a maximum rate loss at temperature of 176°C observed in the DTG curve. The second event (237 - 265 C); corresponding to about 10% mass loss occurs with a maximum rate loss at 247°C. The third event of loss mass is observed in the range 267 - 295°C and corresponds to the loss of the second (ultimate) ligand, occurring with about 16% mass loss at maximum loss rate at 278°C. The fourth event (376 - 443°C) of decomposition suggests the formation of uranyl oxide, U_3O_8 , as the final residue.

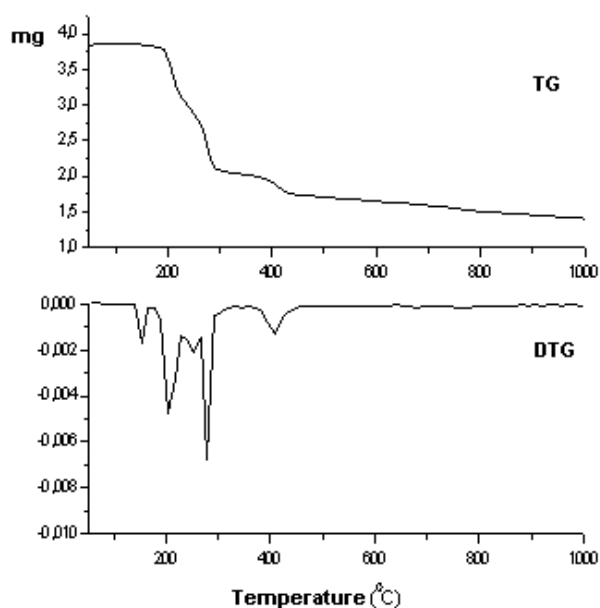


Figure 6. TG and DTG Curves of the Complex $[\text{UO}_2(\text{NO}_3)_2(\text{C}_4\text{H}_8\text{S}_2\text{O})_2]$.

DSC curve presented in the Figure 7 indicates the events associated to the decomposition of the compound. The exothermic peaks in the range of 180 up to 265°C correspond to the first and second events of the TG decomposition, while the endothermic peak observed in the range 252 up to 288°C is associated to the third TG event. The fourth TG event corresponds to the discrete endothermic event that occurs in the range of 400 - 450°C in the DSC curve.

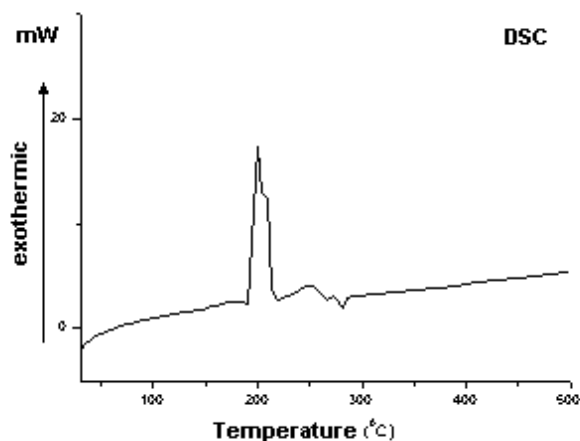


Figure 7. DSC Curve of the Complex $[\text{UO}_2(\text{NO}_3)_2(\text{C}_4\text{H}_8\text{S}_2\text{O})_2]$.

IV. CONCLUSIONS

In this work it was synthesized a new UO_2^{2+} complex. The elemental analysis results and TG data suggested that the complex has the general formula $\text{UO}_2(\text{NO}_3)_2(\text{C}_4\text{H}_8\text{S}_2\text{O})_2$. The TG/DTG data suggested that the fourth event of decomposition produces U_3O_8 , as the final residue. The infrared spectra showed that the DTSO ligands are coordinated to the UO_2^{2+} ion by the oxygen atoms and the NO_3^- ions are bidentate.

The single crystal X-ray defined the final structure of the compound.

The luminescence is assigned to emission from the lowest state $^3\Pi_u$ characteristic of uranyl luminescence spectra. The sequence of absorption, energy-transfer, emission involving distinct absorbing and emitting components is more efficient in 400 nm excitation than in the 290 nm line for the uranyl compound analyzed.

ACKNOWLEDGMENTS

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REFERENCES

- [1] ROSENFELD-GRÜNWALD T. and RABANI, J., **Quantum Yield and electron-transfer reaction of the lowest excited state of uranyl ion**, J. Phys. Chem. Vol 84, p. 2981-2985, 1980.
- [2] TAYLOR, J.C. and MUELLER, M.H., **A neutron diffraction study of uranyl nitrate hexahydrate**, Acta Crystallogr., vol. 19, p. 536-544, 1965
- [3] BAIRD, C.P. and KEMP, T.J., **Luminescence, spectroscopy, lifetimes and quenching mechanisms of excited states of uranyl and other actinide ions**, Progr. Reaction Kinetics, vol. 2, p. 87-139, 1997.
- [4] SUIB, S.L. and CARRADO, K.A., **Zeolite photochemistry: energy transfer between rare-earth and actinide ions in zeolites**, Inorg. Chem., vol. 24, p. 200-202, 1984.
- [5] BLASSE G., GRABMEIER, B.C. Luminescence Material. Springer Verlag, Heidelberg, 1994.
- [6] CARNALL, W.T. in **Gmelin Handbuch der Chemie**, Uranium, Chap10, 1980
- [7] MIRANDA Jr, P., CARVALHO, C.C., ZUKERMAN-SCHPECTOR, J., ISOLANI, P.C., VICENTINI, G. and ZINNER, L.B., **Synthesis and structure of lanthanide(III) picrate complexes with 1,3-dithiane-1-oxide**, J. Alloys Comp., vol. 303-304, p. 162-167, 2000.
- [8] MIRANDA Jr, P., ZUKERMAN-SCHPECTOR, J., ISOLANI, P.C., VICENTINI, G. and ZINNER, L.B., **Hydrated lanthanides picrate complexes with cis-1,3-dithiane-1,3-dioxide (cis-DTSO₂). Structure of the Ho compound**, J. Alloys Comp., vol. 323-324, p. 13-17, 2001.
- [9] AYALA, J.D., ZINNER, L.B., VICENTINI, G., DEL PRA, A. and BOMBIERI, G. **Isomorphous compounds $[\text{Nd}(\text{TDTD})_{1.5}(\text{pic})_3]$ and $[\text{Er}(\text{TDTD})_{1.5}(\text{pic})_3]$ (pic = picrate, TDTD = trans-1,4-dithiane s,s'-dioxide)**, Acta Crystallogr., vol. 50, p 1458-1461, 1994.
- [10] AYALA, J.D., ZINNER, L.B., VICENTINI, G., DEL PRA, A. and BOMBIERI, G., **Synthesis, structure and properties of lanthanide(III) picrate complexes with trans-1,4-dithiane-1,4-dioxide (TDTD)**, Inorg. Chim. Acta., vol. 211, p. 161-166, 1993.
- [11] CARLSON, R.M. Carlson and HELQUIST, P.M., **The synthesis and anionic properties of 1,3-dithiane-1-oxide**, J. Org. Chem., vol. 33, p. 2596-2598, 1968.