



ELSEVIER

Journal of Alloys and Compounds 323–324 (2001) 18–21

Journal of
ALLOYS
AND COMPOUNDS

www.elsevier.com/locate/jallcom

Uranyl nitrate complexes with lactams

A.R. de Aquino^{a,*}, P.C. Isolani^b, J. Zukerman-Schpector^c, L.B. Zinner^b, G. Vicentini^b^aInstituto de Pesquisas Energéticas e Nucleares, C.P. 11049, CEP 05422-970, São Paulo, SP, Brazil^bInstituto de Química, Universidade de São Paulo, C.P. 26077, CEP 05513-970, São Paulo, SP, Brazil^cDepartamento de Química, Universidade Federal de São Carlos, C.P. 676, CEP 13565-905, São Carlos, SP, Brazil

Abstract

The preparation, characterization and spectroscopy of complexes of uranyl nitrate with the lactams: δ -valerolactam (δ -val, C₅H₉NO), ϵ -caprolactam (ϵ -capro, C₆H₁₁NO), 2-azacyclononanone (2-aza, C₈H₁₅NO) and 2-azacyclotridecanone (2-actd, C₁₂H₂₃NO) are described. They were prepared by reaction of hydrated uranyl nitrate with the ligands in ethanolic solution (molar ratio 1:2) and presented the general composition UO₂(NO₃)₂.2L, except for the ϵ -capro complex that is dimeric, with composition: (UO₂)₂(NO₃)₂(O₂)(ϵ -capro)₄. The peroxo bridge was introduced when 2,2-dimethoxypropane contaminated with peroxide was used to precipitate the crystals. They were characterized by CHN microanalyses, IR spectra, TG and DSC analyses and emission spectra in the visible region. The structure of the ϵ -capro complex was determined by X-ray single crystal analysis. © 2001 Published by Elsevier Science B.V.

Keywords: Chemical synthesis; Crystal structure and symmetry; X-ray diffraction; Luminescence; Thermal analysis

1. Introduction

The most common uranium salt is the yellow uranyl nitrate which may have 2, 3 or 6 water molecules depending on whether it is crystallized from fuming, concentrated or diluted nitric acid. The UO₂²⁺ ions (5f⁶6d⁰) are trans-linear. Their most important property is the high solubility in a wide range of organic solvents [1]. This permits the solvent extraction of uranium from aqueous solutions, aided by metal nitrates as 'salting-out agents' to make the extraction more effective by increasing the partition coefficient.

The spectroscopy of uranium compounds, particularly in the case of the uranyl ion has been studied since 1940. Photoexcitation of the uranyl ions leads to a very strong oxidizer, and this fact allowed the operation of a well-succeeded actinometer [2]. Other applications of uranyl photoprocesses include solar collectors [3]; photochemical conversion of solar energy [4], and photocatalysts [5]. Several reviews describe its spectroscopy [6], photophysics and photochemistry [7,8]. Analytical applications of the UO₂²⁺ luminescence resulted in very sensitive and selective methods of the determination of this ion in the environment and geological samples [9].

This paper describes the synthesis, characterization and spectroscopy of uranyl nitrate complexes with the lactams: ϵ -caprolactam (ϵ -capro), δ -valerolactam (δ -val), 2-azacyclononanone (2-aza) and 2-azacyclotridecanone (2-actd). The crystal structure of the ϵ -caprolactam complex was determined by single-crystal X-ray diffraction.

2. Experimental

The compounds were prepared by reaction of hexahydrated uranyl nitrate with the ligands: δ -valerolactam, ϵ -caprolactam, 2-azacyclononanone and 2-azacyclotridecanone in ethanolic solution (molar ratio 1:2). The solutions were left overnight to crystallize. The crystals were separated and dried in vacuo over anhydrous calcium chloride.

They were characterized by CHN elemental analyses using a Perkin-Elmer 240 elemental analyzer; IR Spectra were recorded on a Perkin-Elmer 1750 FTIR spectrometer in Nujol mulls between KBr plates. Emission spectra were recorded on a Hirachi-Perkin-Elmer MPF-4 spectrofluorimeter at room temperature and 77 K. TG and DSC analysis were performed on TGA-50 and DSC-50 Shimadzu apparatus, using sample weights of ca. 3–7 mg, nitrogen

*Corresponding author.

Table 1
Summary of analytical results (%) of the compounds with composition $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{L}$ and $(\text{UO}_2)_2(\text{NO}_3)_2(\text{O}_2)(\epsilon\text{-capro})_4$

L	Carbon		Hydrogen		Nitrogen	
	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.
$\delta\text{-val}$	20.3	20.5	3.1	2.9	9.5	9.1
2-aza	28.4	28.5	4.5	4.5	8.3	8.3
2-actd	36.3	36.6	5.8	5.5	7.1	6.9
$\epsilon\text{-capro}$	25.1	25.3	3.9	3.5	7.3	7.1

atmosphere (50.0 ml min^{-1}) and heating rate of $10^\circ\text{C min}^{-1}$.

3. Crystal structure determination

Data were collected on a CAD-4 Mach 3 Enraf-Nonius diffractometer in the $\omega/2\theta$ scan mode with scan width $\omega=0.80+0.35 \tan \theta$, using graphite monochromated Mo $K\alpha$ radiation ($\lambda=0.71073 \text{ \AA}$) at room temperature (291 K).

Cell parameters were determined on the basis of 25 reflections in the range $9.59 < \theta < 20.87^\circ$. During data collection the intensity of three standard reflections were monitored every 30 min of X-ray exposure time. Data were corrected for Lorentz and polarization effects.

The structure was solved by the standard heavy-atom Patterson method followed by difference Fourier maps. H atoms were located on stereochemical grounds and refined with fixed geometry, each riding on a carrier atom with an isotropic displacement parameter amounting to 1.2 times the value of the equivalent isotropic displacement parameter of the atom to which they are attached. The programs used were SHELXS-86 [10], SHELXL-97 [11] and ZORTEP [12].

4. Results and discussion

Table 1 presents a summary of analytical results for the compounds. The compounds presented the general com-

position $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{L}$ except for the $\epsilon\text{-caprolactam}$, that is $(\text{UO}_2)_2(\text{NO}_3)_2(\text{O}_2)(\epsilon\text{-capro})_4$. The peroxide was introduced when 2,2-dimethoxypropane contaminated with peroxide was used to precipitate the crystals.

Table 2 contains the IR spectra data and shows that νCO is shifted to lower frequencies as compared with the free ligands, indicating coordination through the carbonyl oxygens. The UO_2 symmetric stretching bands were found at ca. 935 cm^{-1} . The frequencies attributed to the nitrate ions in all complexes indicate a C_{2v} symmetry and suggest bidentate coordination.

For all complexes TG and DSC experiments showed the liberation of the ligands and decomposition of uranyl nitrate yielding U_3O_8 as the final residue.

The emission spectra of all complexes consist of a series of bands which are vibronically structured. Fig. 1 presents the emission spectrum of the 2-actd complex at 77 K. This band spectrum is a common feature in uranyl compounds. It is believed that the emitting state is one in which an electron has been transferred from an UO_2^{2+} molecular orbital to a 5f U atomic orbital (charge transfer) [2,13]. A strong argument in favor of this excited state is the pronounced radical like reactivity of these excited molecules [7].

The 2-actd and $\epsilon\text{-capro}$ complexes present at 77 K well-defined vibronic structures, whereas the $\delta\text{-val}$ and 2-aza complexes display broad bands, probably an envelope of vibronic structures. At room temperature, all emission spectra are broad bands. The most intense lines, attributed to zero-phonon transitions [2], at 77 K, appear: in the 2-actd complex, at 490, 512, 535 and 560 nm; in the $\epsilon\text{-capro}$, at 495, 512, 535 and 560 nm; the maxima of the broad peaks in the $\delta\text{-val}$ complex are at 488, 510, 533 and 558 nm; for the 2-aza complex, the vibronic structure is poorly resolved, with the most intense peaks at 492, 509, 533 and 558 nm. The average separations are 837 cm^{-1} (2-actd), 837 cm^{-1} ($\epsilon\text{-capro}$), 843 cm^{-1} ($\delta\text{-val}$) and 840 cm^{-1} (2-aza). The different values for the energy separations suggest some difference in the uranyl immediate environment in these complexes. The zero-phonon lines are magnetic dipole allowed when the U atom is situated in a centrosymmetrical environment [14]. The excitation

Table 2
IR data (cm^{-1}) for the compounds of formula $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{L}$ and $(\text{UO}_2)_2(\text{NO}_3)_2(\text{O}_2)(\epsilon\text{-capro})_4$ ^a

L	νNH	νCO	NO_3^- bands					
			ν_1	ν_2	ν_3	ν_4	ν_6	νUO_2
$\delta\text{-val}$	3344s	1623s	1276s	1028m	755m	1528s	807w	934s
(ligand)	3461s	1664s	—	—	—	—	—	—
2-aza	3347m	1607s	1289s	1035m	732m	1515s	812w	942s
(ligand)	3310s	1650	—	—	—	—	—	—
2-actd	3358	1601	1282s	1026m	746m	1520s	806w	934s
(ligand)	3345	1668s	—	—	—	—	—	—
$\epsilon\text{-capro}$	3344s	1618s	1277s	1028m	755m	1526s	808w	934s
(ligand)	3295s	1695s	—	—	—	—	—	—

^a s, strong; m, medium; w, weak.

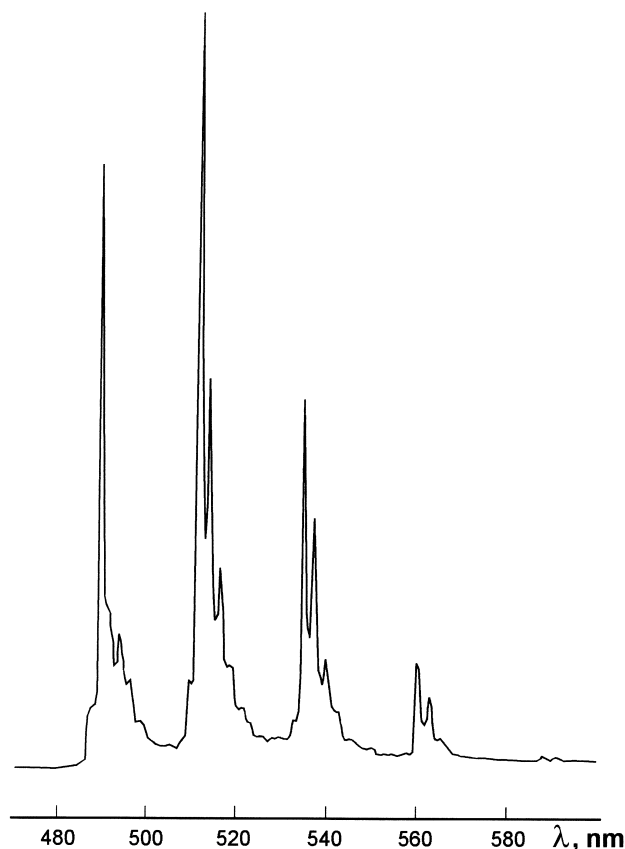


Fig. 1. Emission spectrum of the 2-act complex in the solid state at 77 K.

Table 3
Summary of data collection and crystal parameters

Empirical formula	$C_{12}H_{20}N_3O_8U$
Formula weight	572.34
Crystal system	triclinic
Space group	$P1$
Cell constants	
a (Å)	9.5162(4)
b (Å)	9.7702(5)
c (Å)	11.0076(4)
α (°)	73.775(4)
β (°)	73.685(3)
γ (°)	64.627(4)
Volume V (Å ³)	872.42(7)
Molecules per cell (Z)	2
Density (calcd.) D_c (g cm ⁻³)	2.179
Radiation λ (Mo $K\alpha$) (Å)	0.71073
Crystal size (mm)	0.25 × 0.20 × 0.15
Linear absorption coeff. μ (mm ⁻¹)	9.346
θ range for data collection (°)	2.35–25.49
$h_{min}, h_{max}; k_{min}, k_{max}; l_{min}, l_{max}$	-11, 0; -11, 10; -13, 12
Number of reflections measured	3447
Number of unique reflections	3238 [$R(int)$ = 0.0196]
Number of reflections above $2\sigma(I)$	2790
Refinement method	Full-matrix least-squares on F^2
Number of parameters refined	217
Goodness-of-fit on F^2	1.057
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0293, wR_2 = 0.0728$
R indices (all data)	$R_1 = 0.0429, wR_2 = 0.0780$
Max, min residuals ρ (e Å ⁻³)	0.49 and -0.64

spectra show in all cases broad bands with maxima at 335 and 410 nm.

The crystal structure of the ϵ -caprolactam complex was determined. Table 3 presents a summary of data collection and crystal parameters and Table 4 contains some bond lengths and angles around the uranium atom. Fig. 2 displays an ZORTEP view of the structure. The coordination polyhedra around both U atoms are identical hexagonal bipyramids. For each one, the RMS deviation of the

Table 4
Bond lengths [Å] and angles (°) around the U atoms^a

U–O(1)	1.764(5)
U–O(2)	1.771(5)
U–O(3)	2.312(5)
U–O(3)#1	2.317(6)
U–O(31)	2.409(4)
U–O(21)	2.475(4)
U–O(11)	2.511(5)
U–O(12)	2.537(4)
U–N(11)	2.974(6)
O(3)–O(3)#1	1.473(10)
O(3)–U#1	2.317(6)
O(1)–U–O(2)	177.0(2)
O(1)–U–O(3)	91.2(3)
O(2)–U–O(3)	91.8(3)
O(1)–U–O(3)#1	92.1(3)
O(2)–U–O(3)#1	90.3(3)
O(3)–U–O(3)#1	37.1(2)
O(1)–U–O(31)	93.5(2)
O(2)–U–O(31)	85.64(19)
O(3)–U–O(31)	108.38(18)
O(3)#1–U–O(31)	71.30(17)
O(1)–U–O(21)	90.1(2)
O(2)–U–O(21)	90.90(18)
O(3)–U–O(21)	68.52(17)
O(3)#1–U–O(21)	105.61(17)
O(31)–U–O(21)	175.31(14)
O(1)–U–O(11)	88.8(2)
O(2)–U–O(11)	89.1(2)
O(3)–U–O(11)	133.33(17)
O(3)#1–U–O(11)	170.39(15)
O(31)–U–O(11)	118.21(15)
O(21)–U–O(11)	64.81(14)
O(1)–U–O(12)	89.1(2)
O(2)–U–O(12)	87.9(2)
O(3)–U–O(12)	176.33(16)
O(3)#1–U–O(12)	139.23(17)
O(31)–U–O(12)	67.96(16)
O(21)–U–O(12)	115.14(15)
O(11)–U–O(12)	50.33(15)
O(1)–U–N(11)	88.8(2)
O(2)–U–N(11)	88.3(2)
O(3)–U–N(11)	158.72(18)
O(3)#1–U–N(11)	164.15(16)
O(31)–U–N(11)	92.85(16)
O(21)–U–N(11)	90.20(15)
O(11)–U–N(11)	25.40(14)
O(12)–U–N(11)	24.93(15)
O(3)#1–O(3)–U	71.6(4)
O(3)#1–O(3)–U#1	71.2(4)
U–O(3)–U#1	142.9(2)

^a Symmetry transformation used to generate equivalent atoms: #1 – $x+2, -y, -z+1$.

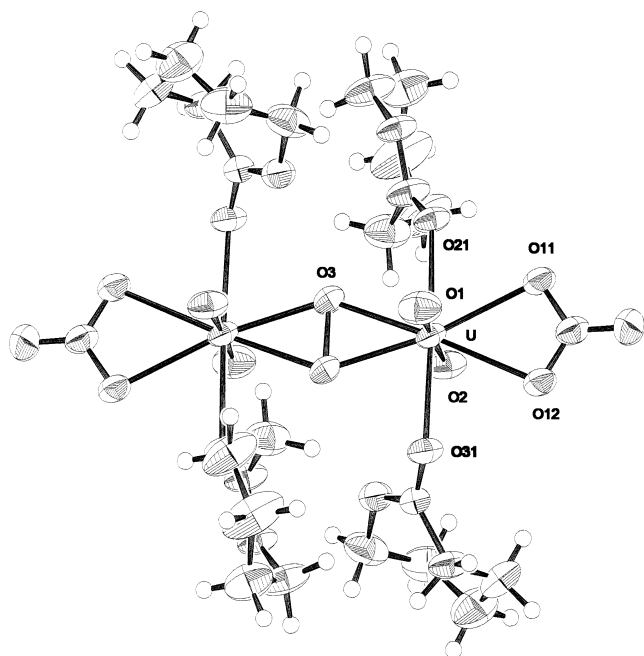


Fig. 2. ORTEP view of ϵ -caprolactam complex.

seven atoms, including U, from the best least-squares plane through them is 0.032. The uranyl O atoms occupy the axial positions, that is, are the apexes of the bipyramid. The peroxo group forms the shared edge uniting the two bipyramids.

Acknowledgements

The authors are indebted to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and

Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) for financial support of this project.

References

- [1] A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 3rd Edition, Wiley, New York, 1972.
- [2] C.P. Baird, T.J. Kemp, *Progr. Reaction Kinetics* 22 (1997) 87.
- [3] G. Folcher, N. Keller, J. Paris, *Solar Energy Mater.* 10 (1984) 303.
- [4] C.K. Jørgensen, R. Reisfeld, *Struct. Bonding (Berlin)* 50 (1982) 121.
- [5] S.L. Suib, K.A. Carrado, *Inorg. Chem.* 24 (1984) 200.
- [6] E. Rabinovitch, R.L. Belford, *Spectroscopy and Photochemistry of Uranyl Compounds*, Pergamon Press, Oxford, 1964.
- [7] H.D. Burrows, T.J. Kemp, *Chem. Soc. Rev.* 3 (1974) 179.
- [8] H. Güsten, *Gmelin Handbook of Inorganic Chemistry*, Vol. A6, Springer-Verlag, Berlin, 1983.
- [9] C. Moulin, P. Decambox, V. Moulin, J.G. Decaillon, *Anal. Chem.* 67 (1995) 348.
- [10] G.M. Sheldrick, *SHELXS-86. Program for the Solution of Crystal Structures*, University of Göttingen, Germany, 1990.
- [11] G.M. Sheldrick, *SHELXL-97. Program for Refinement of Crystal Structures*, University of Göttingen, Germany, 1995.
- [12] L. Zsolnai, *ZORTEP. An Interactive Molecular Graphics Program*. University of Heidelberg, Germany, 1995.
- [13] C.K. Jørgensen, *J. Luminesc.* 18 (1979) 63.
- [14] P.A. Tanner, *Appl. Spectr.* 47 (1993) 1949.