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Uranyl nitrate complexes with diphenylsulfoxide and dibenzylsulfoxide: characterization, luminescence and structures

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Abstract

Uranyl nitrate complexes with diphenylsulfoxide (DPSO) and dibenzylsulfoxide (DBSO) were synthesized and characterized by CHN elemental analyses, infrared absorption spectra, X-ray powder diffraction, visible luminescence spectra and thermal analyses (TG and DTG). The complexes present the compositions $UO_2(NO_3)_2(DPSO)_2$ and $UO_2(NO_3)_2(DBSO)_2$. Infrared spectra show a shift of νSO to lower frequencies, indicating bonding through the sulfoxide oxygen. The nitrate bands indicate that they are coordinated as bidentate ligands. In both complexes thermal decomposition yields U_3O_8 as final product. Both complexes present a strong green luminescence, both at room temperature and 77 K, presenting four bands with vibronic structures partially resolved at low temperature.

The X-ray powder patterns of these complexes are different, therefore, both structures were determined by single-crystal X-ray diffraction. In both complexes the U(VI) occupies a symmetry center. Uranyl oxygen atoms, nitrate ions and neutral ligands are perpendicular with respect to each other.

Keywords: Uranyl; Nitrate; Diphenylsulfoxide; Dibenzylsulfoxide

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1. Introduction

Several applications of uranyl photoprocesses include solar collectors [1], photochemical conversion of solar energy [2] and photocatalyses [3,4]. Some reviews describe the spectroscopy [5], photophysics and photochemistry of this ion [5–7]. The emission of the uranyl ion was used for the determination of this ion in the environment and geological samples [8].

In this article the strong luminescence of the sulfoxide complexes were studied together with thermal analyses and the structures of both compounds.

2. Experimental

The complexes were prepared by reaction of uranyl nitrate, $UO_2(NO_3)_2 \cdot 6H_2O$ (Merck) dissolved in ethanol and treated with diphenylsulfoxide or dibenzylsulfoxide (Aldrich) also dissolved in ethanol (molar ratio 1:2). The adducts were filtered and dried in vacuo over anhydrous calcium chloride.

Microanalytical procedures were performed on a Perkin-Elmer 240 apparatus. Anal.Calc. for $C_{24}H_{20}N_2O_{10}S_2U$(1): C, 36.1; H, 2.5; N, 3.5. Found C, 36.3; H, 2.5; N, 3.4; for $C_{28}H_{28}N_2O_{10}S_2U$(2): C, 39.3; H, 3.3; N, 3.3. Found C, 39.7; H, 3.2; N, 3.2. Infrared absorption spectra were recorded on a Nicolet FTIR-810 spectrometer using Nujol mulls between KBr plates. Emission spectra were obtained at room temperature and 77 K on a Hitachi Perkin-Elmer MPF4 spectrofluorimeter. TG, DTG analyses were performed on a Shimadzu TGA-5 thermobalance, using dynamic air atmosphere (50 mL min^{-1} flow) and 10°C min^{-1} heating rate. X-ray powder patterns were determined on a Rigaku Miniflex diffractometer, using Cu$K\alpha$ radiation.

2.1. X-ray measurements and structure determination

Crystal data collection and final refinement parameters for $UO_2(NO_3)_2(DPSO)_2$ and $UO_2(NO_3)_2(DBSO)_2$

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Table 1
Crystal data and structure refinement

Empirical formula	$C_{24}H_{20}N_2O_{10}S_2U$	$C_{28}H_{28}N_2O_{10}S_2U$
Formula weight	798.56	854.68
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system/space group	Monoclinic/$P2_1/n$	Triclinic/P-1
Unit cell dimensions		
a (Å)	5.8074(9)	9.1816(9)
b (Å)	17.093(1)	9.4468(9)
c (Å)	14.259(1)	9.9736(9)
α (deg)	90	115.82(1)
β (deg)	97.926(8)	93.68(1)
γ (deg)	90	92.33(2)
Volume (Å^3)	1401.9(3)	774.9(1)
Z, Calculated density (mg/m^3)	2/1.892	2/1.839
Absorption coefficient (μ)mm^{-1}	5.994	5.429
$F(000)$	764	414
Crystal size (mm)	$0.30 \times 0.25 \times 0.25$	$0.35 \times 0.24 \times 0.15$
θ (deg) range for data collection	2.38 to 25.5	2.23 to 25.5
Limiting indices	$-7 \leqslant k \leqslant 6$, $0 \leqslant k \leqslant 20$, $0 \leqslant l \leqslant 17$	$-11 \leqslant k \leqslant 11$, $-11 \leqslant k \leqslant 10$, $0 \leqslant l \leqslant 12$
Reflections collected/unique	5607/2591 ($R_{int} = 0.0512$)	3071/2877 ($R_{int} = 0.0421$)
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2
Data/restraints/parameters	2591/0/178	2877/0/196
Goodness-of-fit on F^2	0.962	1.064
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0507$, $wR2 = 0.1310$	$R1 = 0.0373$, $wR2 = 0.0841$
R indices (all data)	$R1 = 0.1150$, $wR2 = 0.1575$	$R1 = 0.0505$, $wR2 = 0.0879$
Largest diff. Peak and hole (e Å^{-3})	2.060 and −1.976	1.207 and −1.045

compounds are reported in Table 1. Reflections were collected using an Enraf-Nonius CAD4 Mach3 diffractometer, using graphite-monochromated Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å). The orientation matrix and cell dimensions were determined by least-square refinement of the angular positions of 25 reflections. Intensity data were collected at room temperature. Three standard reflections were monitored every 2 h. The diffracted intensities were corrected for Lorentz polarization and absorption [9]. The positions of the heavy atoms were obtained from Patterson syntheses [10]. All non-H atoms were located in the subsequent Fourier maps. Structures were refined by full-matrix least-square using anisotropic temperature factors for all non-hydrogen atoms. Hydrogen atoms were introduced at calculated positions in their described geometries and during refinement were allowed to ride on the attached carbon atoms with fixed isotropic thermal parameters (1.2 U_{eq}. of the parent carbon atom). Calculations were performed with the SHELXL-97 program [11], using the scattering factors enclosed therein. The program for the ZORTEP drawing was taken from Ref. [12].

3. Results and discussion

Microanalytical results indicate the general composition $UO_2(NO_3)_2(L)_2$ (L = DPSO and DBSO).

Table 2
Selected infrared frequencies of the ligands and complexes (cm^{-1})

Compounds	ν_4	ν_1	ν_2	ν_6	ν_3	νSO	νUO_2
[$UO_2(NO_3)_2$ (DPSO)]	1526 s	1278 s	1030 m	—	746 m	936 s	957 s
DPSO	—	—	—	—	—	996 m	—
[$UO_2(NO_3)_2$ (DBSO)]	1504 s	1289 s	1030 s	810 m	747 s	941 s	971 s
DBSO	—	—	—	—	—	919 m	—

Infrared absorption data are presented in Table 2. The results indicate that the sulfoxides are bonded to the uranyl ion through the oxygen since a shift of νSO to lower frequencies occurs. The bands of the nitrate ions are indicative that they are coordinated as bidentate in both complexes [13,14].

The emission spectra at room temperature of DPSO and DBSO complexes contain four broad bands, vibronically structured at 492, 512, 537, 562 and 498, 517, 540, 566 nm, respectively. Both complexes are luminescent at 77 K, showing a strong green emission spectra with maximum near 510 nm. The vibronic structures are partially resolved at this temperature. Fig. 1 contains the emission spectrum of the DPSO complex at room temperature and at 77 K. The emission spectra of uranyl compounds come from an excited state in which an electron has been transferred from an UO_2^{2+} molecular orbital to a 5f U atomic orbital [15–18]. The

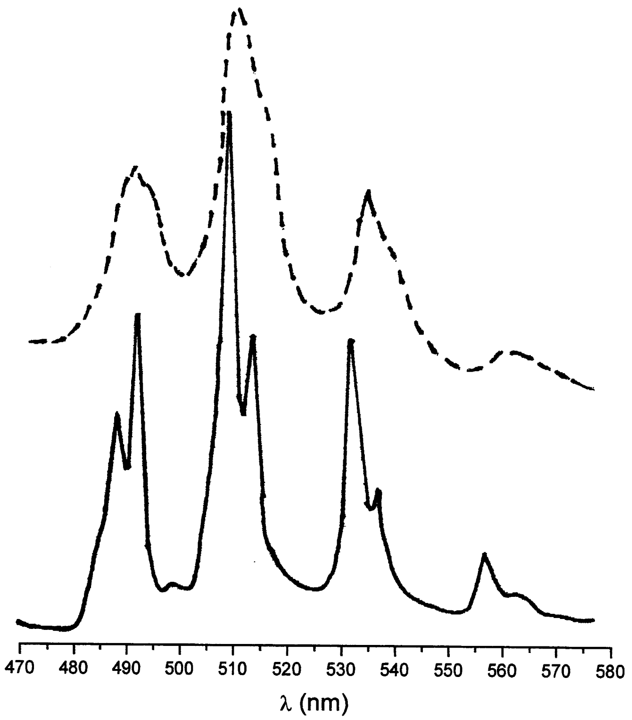

Fig. 1. Emission spectra of the DPSO complexes, at room temperature (dashed line) and at 77 K (solid line).

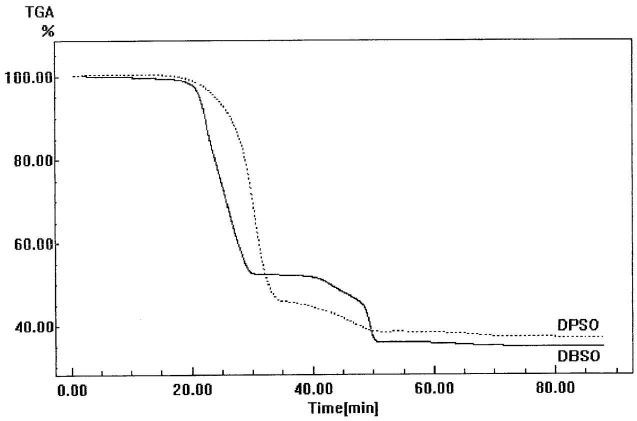

Fig. 2. TG curves of the DPSO and DBSO complexes.

different separations of vibronic bands for the complexes reflect differences in the uranyl immediate environments in the two crystal systems.

Fig. 2 contains the TG curves of the complexes. TG data are found in Table 3. The values obtained for the residues are indicative of formation of U_3O_8.

X-ray powder patterns indicated that the DPSO and DBSO complexes are not isomorphous, therefore both structures were determined by single-crystal X-ray diffraction. The uranium atom is eight-coordinated and the linear uranyl group is equatorially linked to two *trans* bidentate nitrates and to the oxygens of the neutral ligands. The $UO_2(NO_3)_2(L)_2$ units lie on a crystallographic inversion center in both compounds. Table 4 show selected bond lengths and angles for the complexes. Tables 5 and 6 contain the atomic coordinates and equivalent isotropic displacement parameters. Figs. 3 and 4 display perspective views of both complexes.

Table 4
Selected bond lengths (Å) and angles (deg)

$C_{24}H_{20}N_2O_{10}S_2U$		$C_{28}H_{28}N_2O_{10}S_2U$	
U–O(1)	1.747(7)	U–O(1)	1.737(4)
U–O(2)	2.370(11)	U–O(1S)	2.376(4)
U–O(3N)	2.505(8)	U–O(1N)	2.538(5)
U–O(1N)	2.531(9)	U–O(2N)	2.547(5)
O(1)#–U–O(2)	90.6(3)	O(1)–U–O(1S)#	88.38(19)
O(1)–U–O(2)	89.4(3)	O(1)–U–O(1S)	91.62(19)
O(1)–U–O(3N)#	93.3(3)	O(1)–U–O(1N)#	92.7(2)
O(2)–U–O(3N)#	66.7(3)	O(1S)–U–O(1N)#	114.96(15)
O(1)–U–O(3N)	86.7(3)	O(1)–U–O(1N)	87.3(2)
O(2)–U–O(3N)	113.3(3)	O(1S)–U–O(1N)	65.04(15)
O(1)#–U–O(1N)	87.5(4)	O(1)–U–O(2N)	92.3(2)
O(1)–U–O(1N)	92.5(4)	O(1)#–U–O(2N)	87.7(2)
O(2)#–U–O(1N)	116.5(3)	O(1S)#–U–O(2N)	65.94(15)
O(2)–U–O(1N)	63.5(3)	O(1S)–U–O(2N)	114.06(15)
O(3N)#–U–O(1N)	129.7(3)	O(1N)#–U–O(2N)	130.50(15)
O(3N)–U–O(1N)	50.3(3)	O(1N)–U–O(2N)	49.50(15)
$(\# = -x, -y, -z)$		$(\# = -x, -y, -z)$	

Table 3
Results from TG/DTG curves of the compounds with composition $UO_2(NO_3)_2 \cdot 2L$ (L = DPSO and DBSO)

	TG			DTG Peak temp. (°C)	Attribution
	Temp. range (°C)	Weight loss			
		Theor. (%)	Exp. (%)		
DPSO	29–347	50.7	51.2	323	2DPSO
	347–900	11.5	12.0	477	$2NO_2$
	900	35.1	36.8		U_3O_8
DBSO	27–480	53.9	53.3	241,	2DBSO
	480–900	12.6	12.8	276,444	$2NO_2 + \frac{1}{2}O$
	900	32.8	33.9	512	U_3O_8

Table 5
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor (DPSO complex)

	x	y	z	U_{eq}
U	0	0	0	28(1)
S	4342(6)	277(2)	1927(2)	38(1)
N	−2889(16)	1411(6)	61(8)	36(2)
O(1)	2177(11)	561(5)	−405(6)	38(2)
O(2)	1664(14)	267(6)	1580(7)	45(2)
O(1N)	−1611(17)	1167(6)	787(7)	51(3)
O(2N)	−4160(20)	1975(7)	106(8)	65(3)
O(3N)	−2795(14)	1031(5)	−692(6)	39(2)
C(11)	4830(20)	1190(8)	2537(10)	40(3)
C(12)	3120(30)	1731(8)	2486(12)	52(4)
C(13)	3630(30)	2438(9)	2958(14)	65(5)
C(14)	5750(30)	2564(9)	3447(13)	64(5)
C(15)	7490(30)	2020(11)	3510(12)	74(6)
C(16)	7050(30)	1320(11)	3007(11)	59(4)
C(21)	4840(30)	−396(8)	2875(12)	52(4)
C(22)	6490(30)	−905(11)	2872(14)	74(6)
C(23)	6980(50)	−1445(14)	3650(20)	110(9)
C(24)	5500(40)	−1469(13)	4309(17)	100(8)
C(25)	3760(50)	−941(17)	4271(15)	117(9)
C(26)	3380(40)	−398(14)	3575(14)	92(7)

Table 6
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor (DBSO complex)

	x	y	z	U_{eq}
U	0	0	0	33(1)
S	6560(2)	206(2)	1506(2)	40(1)
N	11948(7)	−315(8)	2336(7)	56(2)
O(1)	10701(5)	1938(5)	614(5)	50(1)
O(1N)	10770(5)	292(7)	2603(5)	63(1)
O(2N)	12314(6)	−741(7)	1013(6)	64(2)
O(3N)	12738(7)	−487(10)	3261(7)	88(2)
O(1S)	8157(5)	800(6)	1695(5)	46(1)
C(1)	5606(7)	2008(8)	2363(7)	46(2)
C(2)	6163(7)	3089(7)	3946(7)	41(2)
C(3)	5441(7)	3105(8)	5129(7)	46(2)
C(4)	5948(8)	4124(9)	6569(8)	54(2)
C(5)	7158(9)	5135(9)	6857(9)	60(2)
C(6)	7865(9)	5161(9)	5692(10)	64(2)
C(7)	7381(7)	4120(8)	4234(8)	50(2)
C(11)	6399(8)	−599(9)	2834(8)	50(2)
C(12)	7257(8)	−2026(8)	2393(7)	45(2)
C(13)	8543(9)	−1961(10)	3200(10)	63(2)
C(14)	9361(11)	−3260(13)	2782(13)	85(3)
C(15)	8898(13)	−4610(12)	1521(14)	88(3)
C(16)	7644(13)	−4705(10)	722(10)	74(3)
C(17)	6805(10)	−3402(9)	1140(8)	60(2)

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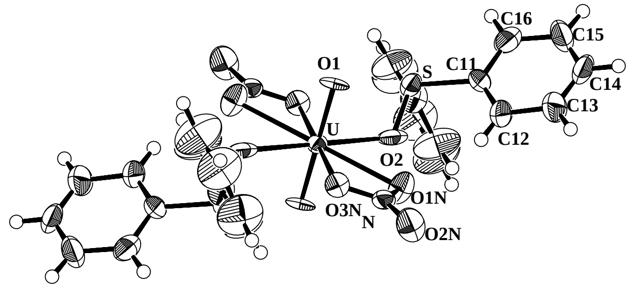

Fig. 3. Structure of the DPSO complex.

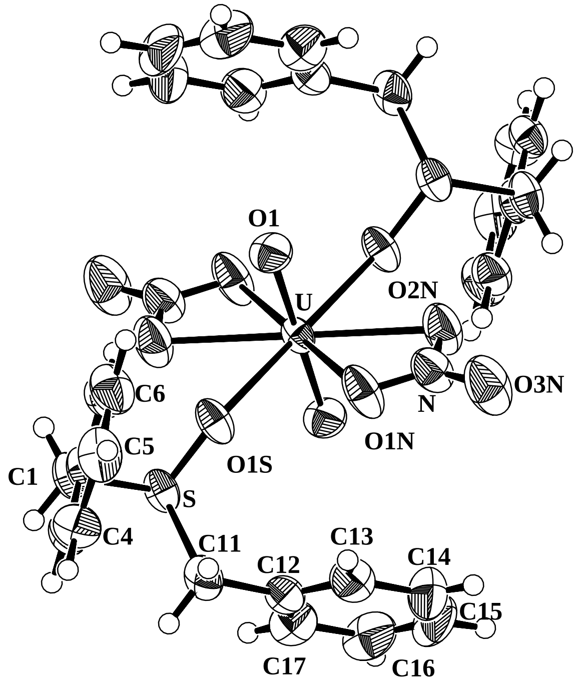

Fig. 4. Structure of the DBSO complex.

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