Dioxouranium(VI) Complexes with γ-Disulfoxides*

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Coordination compounds formed by interaction between dioxouranium(VI) nitrate with γ-disulfoxides were investigated: 1,2-bis(ethylsulfinyl)ethane (bese), 1,2-bis(propylsulfinyl)ethane (bpse) and 1,2-bis(phenylsulfinyl)ethane (bfse), all in the *meso* form.

The ligands bese and bpse were prepared by the oxidation of the corresponding disulfides with dimethylsulfoxide, catalysed by HCl, according to the method described by Hull and Bargar [1]. The ligand bfse was obtained through the oxidation by hydrogen peroxide of the corresponding disulfide, synthesized from the reaction between thiophenol and 1,2-dibromoethane, according to Bell and Bennett [2]. All these disulfoxides and disulfides were analysed by IR and NMR spectra. The dioxouranium(VI) nitrate was used as supplied.

The syntheses of these coordination compounds were carried out from the interaction between the dioxouranium(VI) nitrate and the γ-disulfoxide (bese, bpse or bfse), in the molar ratio 1:2, in a methanolic medium and at room temperature. From the elemental analyses of the obtained solids it was possible to suggest the formula $UO_2(NO_3)_2 \cdot L$, where L is the ligand bese, bpse or bfse. All these compounds are air- and light-stable and can be handled with no special precautions.

The IR spectra of the complexes showed the absence of water and revealed a shift of the (S=O) stretching towards lower frequency, compared with the corresponding free sulfoxide, thus providing evidence for the oxygens being the donor atoms in the coordination. The absorption bands of the uranyl skeleton, in the compounds, occur just in the region mentioned by Bullock [3]. The presence of the band at 840 cm^{-1}, in the bpse derivative, is indicative of non-linearity of the O–U–O group. The corresponding bands of the nitrate ions suggest a bidentate coordination [4]. All these data are shown in Table I.

The thermogravimetric curves were recorded for all three complexes and showed similarity between those of bese and bpse derivatives, which exhibited only one decomposition step. These curves were obtained in the temperature range 30° to 900 °C in N_2 and air atmospheres. Their thermal behavior was seen to be independent of the environment. The final content of U_3O_8 was within the limit of experimental error and is consistent with the proposed formulae (see Table II).

The fluorescence spectra, recorded at room temperature in the range of 450 to 600 nm, showed similarity between all the compounds, with the occurrence of three strong bands at approximately 490, 510 and 533 nm, another of medium intensity near 558 nm and another one of weak intensity at about 586 nm. The strongest band at about 510 nm of $UO_2(NO_3)_2 \cdot L$, which occurs from 509.1 nm up to 511.6 nm, may suggest that the crystal field decreases in the order: bpse > bfse > bese.

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TABLE I. Main IR Absorptions (cm^{-1}) for the $UO_2(NO_3)_2 \cdot L$ Complex[a]

Compounds	ν(S=O)	UO_2^{2+}			NO_3^-					
		ν_3	ν_1	ν_2	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
bese	1040m									
$UO_2(NO_3)_2 \cdot$bese	945m	928m		248s	1265m 1240m	1025m	745m	1525m	695sh	805w
bpse	1010s									
$UO_2(NO_3)_2 \cdot$bpse	940m	920m	840w	256s	1260m 1228w	1020m	745m	1535m	695sh	805w
bfse	1040m									
$UO_2(NO_3)_2 \cdot$bfse	960m	930m		256s	1270m 1200w	1025m	740w	1520m	700sh	805w

[a]s = strong, m = medium, w = weak, sh = shoulder.

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TABLE II. Thermogravimetric Data for the $UO_2(NO_3)_2$·L Complex

Compounds	Sample (mg)	Temperatures[a]		Atmosphere	Rate (°C/min)	Δ[b]	Residue	
		T_i	T_f				Expected	Observed
$UO_2(NO_3)_2$·bese	10.470	26.22	897.68	air	10.0	51.723	48.704	48.300
	10.378	25.88	895.21	N_2	10.0	52.898	48.704	47.113
$UO_2(NO_3)_2$·bpse	5.460	26.13	894.92	air	10.0	54.134	46.443	45.836
	7.569	24.06	894.36	N_2	10.0	55.531	46.443	44.464
$UO_2(NO_3)_2$·bfse	8.827	25.75	895.69	air	10.0	60.333	41.744	39.664
	10.442	25.71	890.47	N_2	10.0	55.846	41.744	44.174

[a] T_i, T_f = initial and final temperatures. [b] Δ = weight loss (%).

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References

1 C. M. Hull and G. Bargar, *J. Org. Chem., 40,* 3152 (1975).
2 E. V. Bell and G. M. Bennett, *J. Chem. Soc.,* 3189 (1928).
3 J. I. Bullock, *J. Inorg. Nucl. Chem., 29,* 2257 (1967).
4 M. R. Rosenthal, *J. Chem. Educ., 50,* 331 (1973).