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Uranyl tropolonate complexes

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THE ABILITY of tropolone (2-hydroxy-2,4,6 cycloheptatrien-l-one) to form very stable complexes with the uranyl ion is well known[1–3]. The present investigations were carried out in order to isolate and characterize these uranyl tropolonates. Dutt and Singh[2] have established that uranyl ion combines with tropolone in the ratios of 1 : 1, 1 : 2 and 1 : 3. However, our work has resulted only in the isolation of the 1 : 2 and 1 : 3 complexes in the solid state.

EXPERIMENTAL

Preparation of UO_2T_2. A reddish-orange compound with the formula UO_2T_2 (T = tropolone anion) was isolated from a reaction in methanol between stoichiometric amounts of uranyl salts (nitrate, chloride, acetate and perchlorate) and tropolone. The precipitate was filtered, washed with methanol, and dried under vacuum at 80°C. The compound was soluble in dimethyl sulfoxide (DMSO) and N,N-dimethylformamide (DMF) but was only slightly soluble in other common organic solvents. Analytical data calculated for UO_2T_2: C, 32·8; H, 2·0; U, 46·5; mol. wt. 512·3. Found: C, 32·7; H, 2·0; U, 48·1; mol. wt. 480 (DMSO solution by vapor pressure osmometry). The density obtained by the flotation method was 2·26 g/cc. An X-ray powder pattern for this compound is presented in Table 1.

Table 1. X-ray powder pattern for UO_2T_2

d, Å	*I*	*d*, Å	*I*
8·24	w−	2·50	w−
7·61	w+	2·39	w−
7·14	w−	2·29	w−
6·81	s	2·15	w−
6·43	w−	2·08	m+
6·09	s+	2·02	w+
5·69	w−	1·96	w
5·25	w+	1·88	w
5·00	w−	1·85	w−
4·67	m−	1·80	m
4·47	m−	1·69	w
4·09	m+	1·64	w−
3·89	w+	1·57	w
3·70	w	1·51	w−
3·46	m	1·46	w−
3·36	s−	1·43	w−
3·21	w	1·40	w−
3·13	w−	1·35	w−
3·01	w−	1·31	w−
2·95	w	1·29	w+
2·84	w+	1·23	w−
2·77	w+	1·20	w−
2·66	w	1·11	w+
2·60	w	1·07	w−

1. B. E. Bryant, W. C. Fernelius and B. E. Douglas, *J. Am. chem. Soc.* **75**, 3784 (1953).
2. Y. Dutt and R. P. Singh, *J. Indian chem. Soc.* **42**, 767 (1965).
3. D. Dyrssen, *Acta chem. scand.* **9**, 2 (1955).

Preparation of UO_2T_2·HT. A yellow-orange compound with the formula UO_2T_2·HT was prepared by reacting uranyl salts and tropolone in methanol in molar ratios of 1 : 4. The precipitate was filtered, washed several times with methanol, and dried under vacuum at 80°C. The compound was soluble in DMSO and DMF but only slightly soluble in other common organic solvents. Analytical data calculated for UO_2T_2·HT: C, 39·8; H, 2·5; U, 37·5; mol. wt. 634·4. Found: C, 39·9; H, 2·6; U, 37·9; mol. wt. 347 (DMSO solution by vapor pressure osmometry). The density obtained by the flotation method was 2·14 g/cc. An X-ray powder pattern for this compound is given in Table 2.

Table 2. X-ray powder pattern for UO_2T_2·HT

d, Å	*I*	*d*, Å	*I*
8·04	s	2·28	w+
6·79	w	2·22	w
6·31	s+	2·12	w+
5·58	m	2·04	w+
5·10	m	1·95	w
4·56	m+	1·88	m−
4·26	m+	1·85	m−
4·07	s−	1·78	w+
3·78	m+	1·74	w−
3·57	s−	1·68	w−
3·38	w	1·63	w−
3·28	w	1·58	w−
3·15	w+	1·55	w−
2·95	w+	1·52	w+
2·79	w−	1·50	w−
2·69	w+	1·48	w−
2·59	m	1·46	w−
2·50	w−	1·43	w−
2·45	w−	1·40	w−
2·38	w	1·31	w−

Infra-red spectra were obtained with a Beckman IR-12 spectrophotometer. The solid spectra were obtained by the potassium bromide and cesium iodide pellet techniques; a potassium bromide cell was used to obtain solution spectra.

Raman spectra were obtained using a Cary 81 Laser-Raman spectrometer.

Molecular weights were measured with a Hitachi Perkin-Elmer molecular weight apparatus using DMSO as the solvent and benzil as the standard.

RESULTS AND DISCUSSION

Solid uranium(VI) tropolonates have been prepared with molar ratios of 1 : 2 and 1 : 3. Attempted isolation of the 1 : 1 complex yielded only the 1 : 2 complex. These compounds were prepared in the anhydrous form by drying under vacuum at 80°C. Samples of these compounds exposed to moist air exhibited a hygroscopic behavior. These compounds exhibited a fairly intractable nature with regard to solubility; however, they did not appear to be polymeric. The UO_2T_2 compound dissolved in DMSO exhibited a molecular weight of 480 (512 theoretical) and thus appeared to be monomeric. The UO_2T_2·HT in DMSO exhibited a molecular weight of 347 (634 theoretical), and thus dissociation to the 1 : 2 compound (UO_2T_2) and tropolone is indicated.

Thermogravimetric analysis of the $UC_2T_2\cdot HT$ compound indicated the loss of one molecule of tropolone on heating to 155°C, thus yielding the UO_2T_2 compound. Additional heating of this product or of the originally prepared UO_2T_2 resulted in decomposition to uranium(IV) oxide at 400°C.

Infra-red spectra were very similar for these two compounds. In the solid state a shift was observed in the two strong tropolone bands[4] which occur at 1618 and 1555 cm^{-1} to 1593 and 1517 cm^{-1}, respectively, for the compounds. The major difference in the i.r. was the presence of C-O-H frequencies in the $UO_2T_2\cdot HT$ spectrum. These bands were observed at 1480, 1280 and 753 cm^{-1}.

A comparison of the i.r. spectra in DMSO for these two compounds showed dissociation of the $UO_2T_2\cdot HT$ compound. The solution spectra of the 1 : 3 compound showed band characteristics of free tropolone in addition to the spectra of the 1 : 2 compound. The Raman spectra of the solid compounds exhibited distinct variations. However, because of the limited solubility of these compounds in DMSO and other solvents, the Raman spectra of the solution did not show the presence of free tropolone. A more detailed discussion of the i.r. and Raman spectra of these compounds will be the subject of a future paper.

On the basis of the foregoing information it appears that the UO_2T_2 compound represents a six-co-ordinate uranium(VI) ion. The $UO_2T_2\cdot HT$, however, appears to be seven-co-ordinate in the solid state, but unstable on dissolution with DMSO.

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4. Y. Ikegami, *Bull. chem. Soc. Japan* **36**, 1118 (1963).

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The nature of the compound $KMn(CN)_3$

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WHEN manganese(II) salts react with a limited amount of aqueous cyanide, a dark green precipitate of composition $KMn(CN)_3$ is obtained. It was suggested many years ago that the very low solubility of this compound indicates a structural resemblance to the complex $K_2Fe[Fe(CN)_6]$ and Prussian blue[1], but the validity of this suggestion has never been examined.

The compound, which is very susceptible to both hydrolysis and oxidation, was prepared by mixing solutions of 25 g of manganese chloride tetrahydrate and 24·7 g of potassium cyanide in water freed from oxygen by boiling and then by passing nitrogen through it for an hour; the precipitate was filtered after 2 min, washed with air-free ethanol, acetone, and ether, and dried *in vacuo* over concentrated sulphuric acid. Manganese was determined by bismuthate oxidation and titration with ferrous iron. (Found: Mn = 31·6 per cent. $KMn(CN)_3$ requires Mn = 32·0 per cent.) The magnetic moment of the compound was determined by the Gouy method, the i.r. spectrum by examination of a mull in Nujol prepared in a dry-box under nitrogen, and the X-ray powder pattern by the Guinier method using sodium chloride for calibration.

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1. H. J. Emeléus and J. S. Anderson, *Modern Aspects of Inorganic Chemistry* 1st Edn, p. 140. Routledge and Kegan Paul, London (1938).