Inorganica Chimica Acta, 35 (1979) L347–L348
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Structural Study of Anhydrous Uranyl Diglycolate

B. F. MENTZEN* and H. SAUTEREAU

Laboratoire de Cinétique et Génie Chimiques, Institut National des Sciences Appliquées de Lyon, 20, avenue Albert Einstein, F-69621, Villeurbanne, France

Received April 4, 1979

In the framework of investigations devoted to uranyl carboxylates [1–4] uranyl diglycolate has been examined. $UO_2(CH_2OHCOO)_2$ has been prepared by dissolving $UO_3 \cdot H_2O$ in an aqueous solution with a large excess of glycolic acid [5]. After several days, yellow crystals of prismatic shape are obtained. Chemical analysis agrees with the formula $UO_2(CH_2\text{-}OHCOO)_2$: calculated U: 56.6%, H: 1.44%, C: 11.4%. Found U:54.6%, H: 1.42%, C: 11.0%.

X-ray Study

The first 24 X-ray diffraction lines observed on a powdered specimen are given in Table I. The positions of these lines have been corrected for absorption and film shrinkage, and are in fair agreement with the uncorrected data previously reported by Polonio *et al.* [6]. A preliminary structural study has been performed on an Enraf-Nonius CAD-4 automatic diffractometer. $UO_2(CH_2OHCOO)_2$ crystallizes in the monoclinic space group $P2_1/c$ the unit-cell parameters being a = 7.969(6), b = 7.583(7), c = 16.81(1) Å, β = 123.75(1)°. The diffraction lines represented in Table I could thus have been indexed using the following quadratic form: $10^5 \sin^2\theta = 1353.68\ h^2 + 1033.54\ k^2 + 304.34\ l^2 + 713.26\ hl$. The observed crystal density ρ = 3.248 g cm^{-3} corresponds to four formula-units per unit-cell; accordingly, all the atoms are on general positions.

Infrared Spectroscopy

The infrared absorption spectrum has been recorded at 25 °C in a CsI matrix with a Perkin-Elmer 457 spectrophotometer (4000–250 cm^{-1}). To the best of our knowledge, the i.r. spectrum of solid uranyl diglycolate has not yet been reported. The absorption bands gathered in Table II have been

TABLE I. X-ray Diffraction Pattern of $UO_2(CH_2OHCOO)_2$; CuKα radiation (λ = 1.5418 Å), Debye-Scherrer camera of 360 mm circumference; visually estimated intensities corrected for absorption.

I_{obs}[a]	$10^5 \sin^2\theta_{obs}$	$10^5 \sin^2\theta_{calc}$	d(Å)	hkl
S	1351	1354	6.63	100
VS	2249	2251	5.14	012
vw	2367	2387	5.01	110
w	3352	3370	4.21	$10\bar{4}$
vw	4095	4134	3.81	020
w	4538	4578	3.62	$20\bar{4}$
m	4787	4813	3.52	$21\bar{2}$
m	5013	5031	3.44	112
m	5450	5415	3.30	200
w	6439	6448 6429	3.04	210 $11\bar{5}$
w	7470	7504	2.823	$12\bar{4}$
w	8451	8427	2.650	$22\bar{1}$
m	8720	8712	2.609	$22\bar{4}$
w	9017	9004	2.565	024
w	9498	9485 9527	2.499	202 $31\bar{4}$
m	10094	10110	2.424	114
w	10466	10446	2.381	$13\bar{2}$
m	11280	11255 11280	2.293	$13\bar{3}$ 221
vw	12008	11990 12041	2.222	016 033
w	12639	12628 12637	2.167	$32\bar{4}$ $32\bar{3}$
m	13166	13176 13151	2.123	$23\bar{3}$ $31\bar{7}$
vw	13611	13619 13594	2.088	222 $23\bar{1}$
vvw	14491	14476	2.023	$22\bar{7}$
vw	15079	15091	1.984	026

[a] V, v: very; S: strong; m: medium; w: weak.

TABLE II. Infra-red Spectra of Anhydrous Uranyl Diglycolate.

I_{obs}[a]	cm^{-1}	Assignment
m	3330	$\nu_I(OH)$
m	3020	$\nu_{II}(OH)$
m_{sh}	2925	$\nu(CH_2)$
w	2845	combinations and overtones
w_{sh}	2745	
w_{sh}	2640	
w	2550	

(Continued overleaf)

---

*Present address: Institut de Recherches sur la Catalyse, 79, boulevard du 11 November 1918, F-69626, Villeurbanne, France.

TABLE II. *(continued)*

$\mathrm{vw_{sd}}$	2505	hydrogen bonding
$\mathrm{vw_{sd}}$	2450	
$\mathrm{vw_{sd}}$	1789	$\nu_s + \nu_{as}(UO_2^{++})$
$\mathrm{S_{sd}}$	1607	$\nu(C{=}O)$
$\mathrm{VS_{sh}}$	1564	
$\mathrm{VS_{sh}}$	1558	
$\mathrm{S_{sd}}$	1508	
$\mathrm{S_{sh}}$	1475	$\delta(OH) + \delta(CH_2)$
$\mathrm{S_{sh}}$	1442	
$\mathrm{S_{sh}}$	1403	$\nu(COO)$
$\mathrm{m_{sh}}$	1332	$\rho_w(CH_2)$
$\mathrm{S_{sh}}$	1279	
$\mathrm{w_{sh}}$	1222	$\rho_t(CH_2)$
$\mathrm{S_{sh}}$	1086	$\rho_r(CH_2)$
$\mathrm{S_{sh}}$	1070	
$\mathrm{w_{sh}}$	988	
$\mathrm{VS_{sh}}$	942	$\nu_{as}(UO_2^{++})$
$\mathrm{S_{sd}}$	930	$\nu(C{-}C)$
$\mathrm{w_{sh}}$	857	$\nu_s(UO_2^{++})$
w	805	$\delta(OCO)$
w	720	
w	674	$\rho_w(OCO)$
$\mathrm{m_{sh}}$	578	$\pi(CO)$
$\mathrm{m_{sh}}$	568	
$\mathrm{m_{sh}}$	538	
$\mathrm{w_{sh}}$	438	ring deformation
$\mathrm{w_{sh}}$	341	
m	285	$\delta(UO_2^{++})$ (?)

[a] Visually estimated. V, v: very; S: strong; m: medium; w: weak; sh: sharp; sd: shoulder.

assigned according to the results of Nakamoto *et al.* [7]. The positions of the $\nu_{as}(UO_2)$ and $\nu_s(UO_2)$ respectively located at 942 and 857 cm^{-1}, and of the combination band at 1789 cm^{-1}, enable us to calculate the mean uranium–oxygen distance in the uranyl ion as being 1.73 Å [8]. The weak bands at 2505 and 2450 cm^{-1} are ascribed to hydrogen-bonds, since they are located in the same region for the uranyl diformate monohydrate [1, 9]. The multiplicity of the bands attributed to the glycolate ions indicates the possibility of a different coordination mode for both of them. For transition-metal glycolates, the ν(OH) band is observed at 3000–3100 cm^{-1} [7]. In our case, the existence of two frequencies labelled ν_I(OH)(3330 cm^{-1}) and ν_{II}(OH)(3020 cm^{-1}) in Table II reinforce our previous assumption.

All these observations invalidate the conjectural model lately proposed by Sbrignadello and coworkers [10]. Furthermore, the determination of the crystal structure of $UO_2(CH_2OHCOO)_2$ which is presently in progress (to be published), shows that the coordination polyhedron of uranium atom is a pentagonal bipyramid as in most uranyl carboxylates of known structure.

References

1 B. F. Mentzen, J. P. Puaux, H. Loiseleur, *Acta Cryst., B 33,* 1848 (1977).
2 B. F. Mentzen, J. P. Puaux, H. Sautereau, *Acta Cryst., B 34,* 1846 (1978).
3 B. F. Mentzen, J. P. Puaux, H. Sautereau, *Acta Cryst., B 34,* 2707 (1978).
4 B. F. Mentzen, *Acta Cryst., B 33,* 2546 (1978).
5 G. Courtois, *C. R., 158,* 1688 (1914).
6 J. Polonio, M. A. Olivares, R.M.R. Lopez, *Anales Real Soc. Espan. Fis. Quim., 65,* 213 (1969).
7 K. Nakamoto, P. J. McCarthy, B. Miniatas, *Spectrochim. Acta, 21,* 379 (1965).
8 L. H. Jones, *Spectrochim. Acta, 15,* 409 (1959).
9 A. Navaro, *Ann. Chim., 6,* 349 (1971).
10 G. Sbrignadello, G. Tomat, G. Battiston, P. A. Vigato, O. Traverso, *J. Inorg. Nucl. Chem., 40,* 1647 (1978).