Inorganica Chimica Acta, 28 (1978) 185–188

The Reaction of Uranyl Chloride with Hydrochlorides and Hydrooxalates of Nitrogen-Containing Heterocycles[a]

B. L. KALSOTRA[b] and C. PÁRKÁNYI

Department of Chemistry, The University of Texas at El Paso, El Paso, Texas 79968, U.S.A.

Received September 26, 1977

Nine uranium(VI) complexes of nitrogen-containing heterocycles were prepared by the reaction of uranyl chloride with the corresponding ligand and hydrochloric or oxalic acid in aqueous medium. Under practically identical conditions, two different types of complexes were obtained in both cases. In the chlorine-containing complexes of aromatic azaheterocycles, the chlorine : uranium ratio was 4:1 [(Pyridine$\cdot$*H)*$_2$*UO*$_2$*Cl*$_4$*, (Quinoline*$\cdot$*H)*$_2$*UO*$_2$*Cl*$_4$*, and (Isoquinoline*$\cdot$*H)*$_2$*UO*$_2$*Cl*$_4$*]. The chlorine : uranium ratio in the complexes of saturated heterocycles was 6:1 [(Piperidine*$\cdot$*H)*$_4$*UO*$_2$*Cl*$_6$*, (Piperazine*$\cdot$*H*$_2$*)*$_2$*UO*$_2$*Cl*$_6$*, and (Morpholine*$\cdot$*H)*$_4$*UO*$_2$*Cl*$_6$*]. Analogously, in the oxalate complexes the ratios were 2:1 [(Pyridine*$\cdot$*H)*$_2$*UO*$_2$*(C*$_2$*O*$_4$*)*$_2$ *and (Quinoline*$\cdot$*H)*$_2$*UO*$_2$*(C*$_2$*O*$_4$*)*$_2$$\cdot$*H*$_2$*O] and 3:1 [(Morpholine*$\cdot$*H)*$_4$*UO*$_2$*(C*$_2$*O*$_4$*)*$_3$$\cdot$*3H*$_2$*O]. The complexes were characterized on the basis of their elemental analysis and their infrared spectra were studied.*

Introduction

Uranyl chloride is known to give complexes with alkali metal chlorides [1, 2], quaternary ammonium chlorides [3], oxalic acid [4], and alkali metal and alkaline earth metal oxalates [5]. Also complexes of uranium(IV) with alkali and alkaline earth metal oxalates have been reported [6]. However, there is no reference in the literature concerning the preparation and characterization of uranyl chloride complexes with hydrochlorides and hydrooxalates of nitrogen-containing heterocycles.

We wish to report here the synthesis and characterization of such complexes. These complexes were prepared by the reaction of uranyl chloride with the corresponding hydrochlorides or hydrooxalates of nitrogen-containing heterocycles in aqueous medium. The compounds are insoluble in common organic solvents, such as methylene chloride, chloroform, carbon tetrachloride, carbon disulfide, ether, acetone, benzene, tetrahydrofuran, dioxane, cyclohexane, acetonitrile, and acetic acid. Analytical data on these compounds are summarized in Table I and the details concerning their preparation and some characteristics are given in Table II.

Experimental

Uranyl chloride and the heterocycles used in the work were reagent grade commercial products. Oxalic acid was "Analar" grade. Infrared spectra were recorded in the 4000–600 cm^{-1} region with a Perkin–Elmer model 710A spectrophotometer using nujol mull. Melting points were determined on a Thomas–Hoover capillary melting point apparatus and are uncorrected.

Synthesis of (Morpholine$\cdot$*H)*$_4$*UO*$_2$*Cl*$_6$

Uranyl chloride (1.37 g, 0.004 mol) was dissolved in distilled water (100 ml) and anhydrous hydrogen chloride gas was passed through the solution until it became saturated (2 hr). Morpholine (1.39 g, 0.016 mol) was added and more hydrogen chloride gas was passed through the mixture (about 50 min). The solution was concentrated to 15 ml which upon cooling gave a yellow compound. It was repeatedly washed with acetone and dried. Yield 96.7%, m.p. 158–159 °C. *Anal.* Calcd. for $C_{16}H_{40}Cl_6N_4O_6U$ (835.3): C, 23.01; H, 4.83; Cl, 25.47; U, 28.50. Found: C, 23.17; H, 4.84; Cl, 25.56; U, 28.25%.

(Pyridine$\cdot$H)$_2$UO$_2$Cl$_4$, (Quinoline$\cdot$H)$_2$UO$_2$Cl$_4$, (Isoquinoline$\cdot$H)$_2$UO$_2$Cl$_4$, (Piperidine$\cdot$H)$_4$UO$_2$Cl$_6$, and (Piperazine$\cdot$H$_2$)$_2$UO$_2$Cl$_6$ were prepared in the same manner.

Synthesis of (Pyridine$\cdot$*H)*$_2$*UO*$_2$*(C*$_2$*O*$_4$*)*$_2$

Uranyl chloride (1.02 g, 0.03 mol) was dissolved in distilled water (50 ml) and a solution of 1.15 g of oxalic acid (0.009 mol) and 0.95 of pyridine (0.012

---

[a] Some results of this study were presented at the 33rd Southwest Regional Meeting of the American Chemical Society, Little Rock, Arkansas, December 5–7, 1977.

[b] R. A. Welch Postdoctoral Fellow, 1977–1978. Permanent address: Department of Chemistry, The University of Jammu, Jammu – 180001, India.

TABLE I. Analytical Data on Uranyl Complexes.

Compound	Formula	Mol. Wt.	Analysis							
			Calcd.				Found			
			%C	%H	%Cl	%U	%C	%H	%Cl	%U
$(Pyridine{\cdot}H)_2UO_2Cl_4$	$C_{10}H_{12}Cl_4N_2O_2U$	572.1	20.99	2.11	24.79	41.61	21.15	2.16	24.70	41.33
$(Quinoline{\cdot}H)_2UO_2Cl_4$	$C_{18}H_{16}Cl_4N_2O_2U$	672.2	32.16	2.40	21.10	35.41	32.17	2.39	21.08	35.72
$(Isoquinoline{\cdot}H)_2UO_2Cl_4$	$C_{18}H_{16}Cl_4N_2O_2U$	672.2	32.16	2.40	21.10	35.41	32.24	2.31	20.96	35.50
$(Piperidine{\cdot}H)_4UO_2Cl_6$	$C_{20}H_{48}Cl_6N_4O_2U$	827.4	29.03	5.85	25.71	28.77	30.22	6.15	25.56	28.51
$(Piperazine{\cdot}H_2)_2UO_2Cl_6$	$C_8H_{12}Cl_6N_4O_2U$	659.1	14.58	3.67	32.28	36.11	14.51	3.80	31.85	35.91
$(Morpholine{\cdot}H)_4UO_2Cl_6$	$C_{16}H_{40}Cl_6N_4O_6U$	835.3	23.01	4.83	25.47	28.50	23.17	4.84	25.56	28.25
$(Pyridine{\cdot}H)_2UO_2(C_2O_4)_2$	$C_{14}H_{12}N_2O_{10}U$	606.3	27.73	1.99	–	39.26	27.67	2.09	–	39.38
$(Quinoline{\cdot}H)_2UO_2(C_2O_4)_2{\cdot}H_2O$	$C_{22}H_{18}N_2O_{11}U$	724.4	36.47	2.50	–	32.85	35.73	2.80	–	33.08
$(Morpholine{\cdot}H)_4UO_2(C_2O_4)_3{\cdot}3H_2O$	$C_{22}H_{46}N_4O_{21}U$	940.7	28.09	4.93	–	25.30	28.18	4.84	–	25.22

TABLE II. Synthesis of Uranyl Complexes.

Compound	UO_2Cl_2 Taken (g)	Base Added (g)	Oxalic Acid Added (g)	HCl Gas Passed (hr)	Color	Yield, %	M.p., °C
$(Pyridine{\cdot}H)_2UO_2Cl_4$	1.10	1.00	–	2¼	Yellow	94.0	253.5–256
$(Quinoline{\cdot}H)_2UO_2Cl_4$	1.13	1.68	–	2½	Yellow	69.2	214–215
$(Isoquinoline{\cdot}H)_2UO_2Cl_4$	1.56	2.37	–	3	Yellow	70.5	219
$(Piperidine{\cdot}H)_4UO_2Cl_6$	1.03	1.03	–	2¾	Yellow	96.0	149
$(Piperazine{\cdot}H_2)_2UO_2Cl_6$	1.00	0.51	–	2½	Yellow	98.4	268 (dec.)
$(Morpholine{\cdot}H)_4UO_2Cl_6$	1.37	1.39	–	2¾	Yellow	96.7	158–159
$(Pyridine{\cdot}H)_2UO_2(C_2O_4)_2$	1.02	0.95	1.15	–	Yellow	68.8	306 (dec.)
$(Quinoline{\cdot}H)_2UO_2(C_2O_4)_2{\cdot}H_2O$	1.37	2.07	1.52	–	Yellow	93.0	305 (dec.)
$(Morpholine{\cdot}H)_4UO_2(C_2O_4)_2{\cdot}3H_2O$	1.62	1.66	1.79	–	Yellow	83.5	124 (melts with dec.)

mol) in water (25 ml) was added. The resulting mixture was concentrated to about 20 ml which upon cooling gave a yellow compound. It was further recrystallized from water, washed three to four times with acetone, and dried in air. Yield 68.8%, m.p. 306 °C (dec.). *Anal.* Calcd. for $C_{14}H_{12}N_2O_{10}U$ (606.3): C, 27.73; H, 1.99; U, 39.26. Found: C, 27.67; H, 2.09; U, 39.38%.

$(Quinoline{\cdot}H)_2UO_2(C_2O_4)_2{\cdot}H_2O$ and $(Morpholine{\cdot}H)_4UO_2(C_2O_4)_3{\cdot}3H_2O$ were prepared similarly using the same procedure.

Analyses

Uranium was determined according to the classical method by precipitation as ammonium diuranate and weighed as U_3O_8. Chlorine was determined as silver chloride. Carbon and hydrogen microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Results and Discussion

The method of preparation of complexes of uranyl chloride with cyclic amine hydrochlorides and hydrooxalates is analogous to the preparation of dipyridinium iron(III) pentachloride [7] and of morpholinium and ethylenedimorpholinium oxalato cuprates(II) [8].

The infrared spectra of all these complexes show an intense peak at ~920 cm^{-1} which has been assigned to the asymmetric stretching vibration of the UO_2 group [9, 10]. The oxalate group is characterized by the presence of bands at 1630 and 1445 cm^{-1} due to asymmetric C=O stretching and symmetric C–O stretching vibrations. The absorptions arising from water of crystallization lie at ~3400 cm^{-1} and ~1600 cm^{-1} and are assigned to the stretching ν(O–H) vibration and the bending δ(H–O–H) vibration, respectively [11].

Pyridinium, Quinolinium, and Isoquinolinium Complexes

The presence of pyridinium [12], quinolinium, and isoquinolinium cations in their respective complexes is shown by the peaks observed in their spectra. Thus, the C–H stretching frequency at ~2950 cm^{-1}, the ring stretching vibrations at about 1640, 1595, 1475, and 1370 cm^{-1}, the C–H in-plane deformation at or near 1310, 1280, 1255, 1200, and 1045 cm^{-1}, the ring breathing modes at or near 1010 cm^{-1}, and the C–H out-of-plane deformation at or near 725 cm^{-1} are such bands. The N–H group is characterized by the appearance of a peak at 895 cm^{-1} which corresponds to the N–H stretching (symmetrical) [13] and a strong band at or near 1540 cm^{-1} arising from the N–H bending. Thus, the infrared spectral studies confirm the presence of pyridinium, quinolinium, and isoquinolinium cations in these complexes.

Piperidinium, Piperazinium, and Morpholinium Complexes

Two regions are of particular interest in the infrared spectra of these compounds, *viz.*, a) absorptions between 3000–2500 cm^{-1}, and b) absorptions between 1600–600 cm^{-1}. The first region includes the stretching vibrations of the substituted ammonium ion and the latter includes its deformational modes in addition to the vibrations of the whole skeleton. There are two N–H stretching vibration bands, the symmetrical and asymmetrical vibrations at or near 2850 and 2955 cm^{-1} due to the presence of an NH_2^+ ion, and the band at or near 1590 cm^{-1} corresponds to the bending modes of the NH_2^+ group. Two other bands near 2530 and 2425 cm^{-1} may be connected in some way with the NH_2^+ group as well. Table III shows that there is a relationship between these bands and those assigned to the stretching vibrations. The interpretation of this pair of bands is uncertain. They may arise as difference bands caused by absorption from a low-frequency fundamental vibration near 400 cm^{-1}, or alternatively as vibrations of the NH_2^+ group lowered by hydrogen bonding either with other similar groups or even with residual water in the solid.

Because of the insolubility of these complexes in common organic solvents, we were not able to study their other physical properties.

Acknowledgments

Financial support from the Robert A. Welch Foundation, Houston, Texas (Grant No. AH-461) is gratefully acknowledged. One of the authors (B. L.

TABLE III. Some Bands in the Infrared Spectra of the Uranyl Complexes with Saturated Azaheterocycles.

Compound	Bands (cm^{-1})					
	ν_a	ν_{sym}	Δ	ν_b	ν_{asym}	Δ
$(Piperidine{\cdot}H)_4UO_2Cl_6$	2415	2832	417	2530	2945	415
$(Piperazine{\cdot}H_2)_2UO_2Cl_6$	2430	2850	420	2520	2960	440
$(Morpholine{\cdot}H)_4UO_2Cl_6$	2440	2860	420	2530	2955	425

K.) should like to thank the University of Jammu, Jammu, India, for a leave of absence and the Robert A. Welch Foundation for a postdoctoral research fellowship.

References

1 J. I. Bullock, *J. Chem. Soc. A.*, 781 (1969).
2 J. E. Newbery, *Spectrochim. Acta, Part A, 25,* 1699 (1969).
3 E. Staritzky and J. Singer, *Acta Cryst., 5,* 536 (1952).
4 M. Bideau, R. Bressat, B. Mentzen and A. Navarro, *C. R. Acad. Sci., Ser. C, 271,* 225 (1970).
5 R. N. Shchelokov and V. I. Belomestnykh, *Russ. J. Inorg. Chem. 14,* 1491 (1969).
6 C. Keller, "Chemistry of the Transuranium Elements", Verlag Chemie, Weinheim (1971).
7 R. K. Sharma and N. Kumar, *J. Inorg. Nucl. Chem., 36,* 1172 (1974).
8 M. R. Udupa, *J. Inorg. Nucl. Chem., 38,* 181 (1976).
9 R. J. Magee and L. Gordon, *Talanta, 12,* 445 (1965).
10 V. I. Gaivoronskii, O. A. Osipov and R. R. Shagidullin, *Radiokhimiya, 5,* 244 (1963).
11 K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", 2nd Ed., Wiley–Interscience, New York (1970).
12 A. R. Katritzky and P. J. Taylor, in "Physical Methods in Heterocyclic Chemistry" (A. R. Katritzky, Ed.), Vol. 4, p. 378, Academic Press, New York (1971).
13 D. Cook, *Can. J. Chem., 39,* 2009 (1961).

Note added in proof (March 31, 1978).

The complexes are soluble in water. The electronic absorption spectra of the chloro complexes measured in water exhibit absorption in the 395-420 nm region, with a pronounced fine structure. The oxalato complexes absorb at 395-435 nm. In the ultraviolet region, the spectra of the complexes are similar to those of the protonated heterocyclic ligands.