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Note

Uranylchitosan complexes

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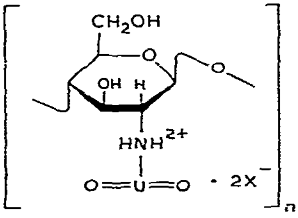
Chitin [(1→4)-linked 2-acetamido-2-deoxy-β-D-glucan] and chitosan, its *N*-deacetylated derivative, display specific binding characteristics. Chitin adsorbs wheat-germ agglutinin[1] and phosphorylases[2], and chitosan[3,4] adsorbs Ti^{3+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Ag^{+}, Cd^{2+}, Zn^{2+}, and Hg^{2+}, but not Li^{+}, Na^{+}, Mg^{2+}, Si^{2+}, K^{+}, and Ca^{2+}. The adsorption of uranium on chitin[5,6], chitosan[7], and their phosphorylated derivatives[8] has also been reported, but little is known about the mechanism and the enhancement of uranyl adsorption by chemical modification of chitosan[9].

We now propose a structure for uranylchitosan and report on the effect of chemical modification of chitosan on uranyl adsorption.



1 X = OH
2 X = OAc
3 X = NO_3

The uranylchitosan complexes **1**–**3** show a strong i.r. absorption at 920 cm^{-1} (U=O). The absorption of chitosan at ~1600 cm^{-1} (NH_2) is split into two bands at ~1630 and ~1530 cm^{-1} in the spectra of **1**–**3** as it is in chitosan salts with AcOH and HNO_3. This fact indicates that the amino groups of chitosan donate lone-pair electrons to uranium atoms to form a co-ordinate complex, as shown in the formulae. The structure is also confirmed by the elemental analyses, in which the molar ratios of C/N and U/N are ~6 and ~1, respectively. Complex **1** had λ_{max} 417 nm (2% AcOH) and $[\alpha]_D^{12}$ +6° (*c* 0.5, 2% acetic acid) {cf. $[\alpha]_D^{17}$ −10° (*c* 1.3, 2% acetic

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TABLE I

RATES OF URANYL ADSORPTION ON CHITOSAN DERIVATIVES[12-14]

N-*Substituent or chitosan derivative*	*D.s.*	*Rate of uranyl adsorption (μg/mg/2 h)*	*Relative rate*
Butyryl	1.0	0	0
2-Nitrobenzylidene	1.0	0	0
3-Nitrobenzylidene	1.0	0	0
3-Hydroxybenzylidene	0.8	1	1
Acetyl	1.0	3	4
2-Chlorobenzylidene	1.0	4	6
4-Nitrobenzylidene	1.0	4	6
Stearoyl	1.0	4	6
4-Methylbenzylidene	0.8	5	7
4-Hydroxy-3-methoxybenzylidene	n.d.[a]	5	7
Benzylidene	1.0	7	10
4-Chlorobenzylidene	1.0	8	12
3,4-Dimethoxybenzylidene	1.0	11	16
4-Hydroxybenzylidene	0.8	11	16
DNP-Chitosan	n.d.[a]	13	19
2-Methylbenzylidene	0.8	15	22
DEAE-*N*-Acetylchitosan	1.0	17	25
Chitin	n.d.[a]	18	26
3-Methylbenzylidene	0.8	20	29
Chitosan acetate	—	20	29
Sulphated *N*-acetylchitosan (SO_4^{2-} 1.5%)[b]	1.0	29	43
DEAE-Chitosan	—	30	44
4-Fluorobenzylidene	0.8	31	46
Phosphorylated chitosan (P 2.7%)[b]	—	38	56
Succinylacetyl (d.s. 0.3 and 0.7)[b]	1.0	39	57
Nicotinylidene	0.5	41	60
Phthaloyl[b]	0.05	51	75
Phosphorylated *N*-acetylchitosan (P 2.2%)[b]	1.0	51	75
CM-*N*-Acetylchitosan[b]	1.0	52	76
Chitosan	—	68	100
(Acetylthio)succinyl[b]	0.6	79	116

[a] Not determined. [b] The derivative contains acidic groups.

acid) for chitosan[10]}, and was soluble in aqueous acid (AcOH and HNO_3), but insoluble in water and in aqueous alkali (NaOH). Uranyl cations were released to the extents of 46, 90, and 97% from uranylchitosan complexes by elution with 0.1M NaOH, NH_4OH, and $(NH_4)_2CO_3$, respectively.

Table I shows the rates of uranyl adsorption for a series of chitosan derivatives. The data indicate that the increases in the degree of *N*-substitution and salt formation cause a decrease in the adsorption rate. Uranyl cations were adsorbed by the *N*-(acetylthio)succinyl derivative at 1.2 times the rate for chitosan, but by other *N*-acyl, *N*-alkylidene, and *N*-arylidene derivatives at lower rates. However, there is no distinct correlation between the rates of uranyl adsorption and the structure of *N*-substituents[9]. The rate of uranyl adsorption on *N*-acetylchitosan was increased by the presence of phosphate, sulphate, and carboxyl groups.

Uranyl adsorption on chitosan was most efficient at pH 7.5, and the recovery by the column method was 1.3 times that for the batch-wise method. Of the uranyl cations added, to a level of 1 p.p.m., to natural water (200 ml of each) of rivers, lakes, and hot springs in the vicinity of a uranium mine, Tottori, Japan, up to 96% of the uranium could be recovered by the column method on chitosan (200 mg) at a flow rate of 50 ml/h (see Experimental). When chitosan (70 g), packed in a polyurethane sack, was immersed in flowing river water for one month, up to 58 μg of uranium was adsorbed. However, the uranyl adsorption was strongly inhibited in sea water.

EXPERIMENTAL

Materials and methods. — Chitosan, $[\alpha]_D^{17}$ −10° (*c* 1.3, 2% acetic acid), prepared[10] from chitin (crab shell) gave no appreciable p.m.r. signal (D_2O–DCO_2D, 9:1) for NAc groups. Uranium was determined by the Arsenazo III method)[11]. The other methods were as cited previously[10].

Uranylchitosan complexes. — The pH of a solution of uranyl nitrate [$UO_2(NO_3)_2 \cdot 6\ H_2O$, 800 mg] in distilled water (150 ml) was adjusted to ~6 with 2M NaOH. Finely powdered chitosan (160 mg) was then added and the suspension was stirred at room temperature for 24 h. The yellow precipitate was collected by centrifugation, washed with distilled water several times, suspended in ethanol (~100 ml), collected, washed with ether, and dried over P_2O_5 at 100° for 2 h *in vacuo*, to give uranylchitosan (**1**; 460 mg, 97%); ν_{max}^{KBr} 3600–3200 (OH and NH), 2900 (CH), 1630 and 1530 (NH_2-U^{2+}), 1180–1000 (C-O), and 920 cm^{-1} (U=O); uranyl–GlcN ratio, 1.0.

Anal. Calc. for $\{(C_6H_{11}NO_4)(UO_2[OH]_2 \cdot 0.61\ H_2O\}_n$: C, 15.13; H, 3.01; N, 2.94; U, 49.99. Found: C, 15.14; H, 2.93; N, 2.92; U, 50.3.

Uranyl acetate [$UO_2(AcO)_2 \cdot 2\ H_2O$, 800 mg], when treated with chitosan (160 mg) without adjustment of pH as described above, gave uranylchitosan$(AcO)_2$ (**2**; 506 mg, 92%) (Found: U, 43.2%; uranyl–GlcN ratio, 1.0).

To an aqueous solution of uranyl nitrate (800 mg) was added chitosan (160 mg). Ethanol (10 vol.) was added to the viscous solution, to give uranylchitosan$(NO_3)_2$ (**3**; 300 mg, 54%) (Found: U, 29.4%; uranyl–GlcN ratio, 0.4).

Rates of uranyl adsorption. — A uranyl solution (200 ml, 6 p.p.m., pH 7.5) was applied to a column (diameter 0.4 cm) of adsorbent (10 mg) at 100 ml/h. The column was washed with distilled water (~2 ml). Uranyl cations were desorbed by elution with 0.1M $(NH_4)_2CO_3$ (10 ml) and determined by the Arsenazo III method[11].

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