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Alkaline Salts of Oxalato Titanate(IV) Complexes. Part 1. Syntheses and Characterizations

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Alkaline salts of Ti(IV) oxalato complexes $M_2[TiO(C_2O_4)_2]\cdot nH_2O$*, where* M = Li, Na, K, Rb, Cs*, have been synthesized. These compounds have been characterized by chemical analyses, infrared spectroscopy and X-ray diffraction.* $Li_2[TiO(C_2O_4)_2]\cdot 4H_2O$ *has a tetragonal unit cell of dimensions* a = b = 14.27(1), c = 11.96(1)Å *and the space group is* $P4_2/n$. $K_2[TiO(C_2O_4)_2]\cdot 2H_2O$ *has a triclinic unit cell:* a = 9.861(5), b = 11.085(6), c = 11.768(7)Å, α = 68.21(4), β = 85.15(4), γ = 76.37(4)° *and the space group is P1. For* $Na_2[TiO(C_2O_4)_2]\cdot 3H_2O$, a = 8.98(1), b = 11.04(1), c = 11.51(1)Å, α = 66.1(1)°, β = 84.5(1), γ = 77.8(1)°. *For* $Rb_2[TiO(C_2O_4)_2]\cdot H_2O$, a = 10.43(1), b = 11.15(1), c = 11.54(1)Å, α = 69.9(1), β = 84.5(1), γ = 75.5(1)°. *Finally for* $Cs_2[TiO(C_2O_4)_2]\cdot H_2O$, a = 10.89(1), b = 11.62(1), c = 12.00(1)Å, α = 68.2(1), β = 85.2(1), γ = 76.0(1)°. *The infrared bands have been assigned by analogy with the assignment of a trisoxalato Cr(III) complex.*

Introduction

The potassium salt of the oxalato titanate(IV) complex was first described in 1893 by Péchard [1]. This water soluble salt is often used as a starting material in the preparation of pure $Ba[TiO(C_2O_4)_2]\cdot 4H_2O$ which is itself used in the preparation of ultrapure barium titanate, $BaTiO_3$, an important ferroelectric material. It was only in 1974 that a structural study of an oxalato titanate(IV) complex was reported [2]. The crystal structure determination of the ammonium salt revealed the existence of a cyclic anion of stoichiometry $[TiO(C_2O_4)_2]_4^{8-}$. We have undertaken the synthesis of all the alkaline salts of the oxalato titanate(IV) complexes in order to establish whether the tetracyclic anion was special to the ammonium salt or was a general feature of these compounds. We report here on the syntheses and the characterizations of the $M_2[TiO(C_2O_4)_2]\cdot nH_2O$ salts where M = Li, Na, K, Rb and Cs.

Experimental

The alkaline salts of the oxalato titanate(IV) complexes were synthesized in a manner similar to that described for the preparation of the ammonium salt [2]. The synthesis is briefly reported below. Dissolve 0.1*M* oxalic acid in 100 ml of an aqueous solution 0.5*M* in $TiCl_4$. Slowly add 50 ml of 0.3*M* solution of the desired base. The solution must be stirred constantly and kept refrigerated to avoid the precipitation of titanium hydroxide. Very slowly pour 150 ml of 95% ethanol onto the surface of the oxalic solution of Ti(IV). The ethanol will diffuse slowly in the solution and after a few hours the salt will crystallize. The crystals are then filtered, washed with ethanol, and dried at room temperature.

The infrared spectra of the oxalato titanate(IV) complexes and of the comparison compound were recorded between 4000 and 250 cm^{-1} on a Perkin–Elmer model 621 spectrophotometer using KBr pellets.

All powder diffraction films were taken in a Debye–Scherrer camera, 114.5 mm in diameter. Nickel filtered CuKα radiation was used throughout (λ Cu$K\bar{\alpha}$ = 1.54178Å). The intensities of the powder lines were visually estimated. Single crystal diffraction films were taken on a precession camera.

In the first synthesis attempts, qualitative tests were used to characterize titanium and oxalate ions. Later, the elemental analyses were carried out by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

Results and Discussion

The elemental analyses confirmed that the $M_2[TiO(C_2O_4)_2]\cdot nH_2O$ complexes had been synthesized. These analytical results are presented in Table I.

X-ray diffraction

The observed and calculated d-spacings and the observed intensities of the powder diffraction lines have been obtained and are presented in Table II. All the powder films were indexed and the unit cell dimensions were computed by least-squares, using the method described by Cohen [3]. These and other crystallographic data are presented in Table III.

TABLE I. Analytical Results for $M_2[TiO(C_2O_4)_2]\cdot nH_2O$.

Cation M		n	M	Ti	O	C	H
Li	found		4.27	14.74	61.79	14.63	2.86
	calculated	4	4.26	14.70	63.84	14.73	2.45
Na	found		13.25	13.62	56.00	13.67	2.84
	calculated	3	13.52	14.09	56.49	14.12	1.76
K	calculated	1	23.25	14.25	47.59	14.28	0.59
	found		23.27	13.72	47.05	13.53	1.52
	calculated	2	22.08	13.52	49.69	13.57	1.14
Rb	found		39.43	10.60	37.27	11.28	1.23
	calculated	1	39.86	11.15	37.31	11.19	0.47
Cs	found		50.00	9.05	30.27	9.06	0.54
	calculated	1	50.75	9.14	30.55	9.17	0.38

TABLE III. Crystal Data for $M_2[TiO(C_2O_4)_2]\cdot nH_2O$ Complexes.

M	Li	Na	K	Rb	Cs	NH4	
						This Work	Ref. 2
n	4	3	2	1	1	1	1
Mw, g	325.84	339.94	354.15	428.89	523.76	294.03	
a, Å	14.27(1)	8.98(1)	9.861(5)	10.43(1)	10.89(1)	13.38(1)	13.473(1)
b	14.27(1)	11.04(1)	11.085(6)	11.15(1)	11.62(1)	11.30(1)	11.329(1)
c	11.96(1)	11.51(1)	11.768(7)	11.54(1)	12.00(1)	17.65(1)	17.646(2)
α, °	90	66.1(1)	68.21(4)	69.9(1)	68.2(1)	90	90
β	90	84.5(1)	85.15(4)	84.5(1)	85.2(1)	126.7(1)	126.66(1)
γ	90	77.8(1)	76.37(4)	75.5(1)	76.0(1)	90	90
V, Å^3	2430.	1019.	1160.	1220.	1368.	2140.	2160.
ρ_c, g cm^{-3}	1.782	2.216	2.028	2.336	2.543	1.826	1.808
ρ_o, g cm^{-3}	1.81	–	2.04	–	2.55	1.79	1.80
Z	8	4	4	4	4	8	
Space Group	$P4_2/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	

$Li_2[TiO(C_2O_4)_2]\cdot 4H_2O$

The precession films obtained with a single crystal of $Li_2[TiO(C_2O_4)_2]\cdot 4H_2O$ indicate that the compound belongs to the tetragonal system, and the systematic absences (hk0, h + k ≠ 2n; h0l, l ≠ 2n) define uniquely the space group $P4_2/n$. The density calculated for the composition $Li_2[TiO(C_2O_4)_2]\cdot 4H_2O$ agrees very well with the observed value, measured by flotation in the mixture CH_3I–CCl_4, when there are 8 $\{Li_2[TiO(C_2O_4)_2]\cdot 4H_4O\}$ formulae per unit cell. One may assume that the anion is present as a tetrameric unit as this was the case for the ammonium salt [2]. Since the general position of the space group $P4_2/n$ is of order 8, there will be two tetrameric anions per unit cell. If this is the case, because the positions of order two have local symmetry $\bar{4}$, the cyclic anion will then have $\bar{4}$ symmetry.

$K_2[TiO(C_2O_4)_2]\cdot 2H_2O$

The water content of this salt is uncertain. The chemical analyses do not point clearly towards one particular degree of hydration. One or two molecules of water could be accounted for by the observed data. Péchard [1] found that the salt has the composition $K_2[TiO(C_2O_4)_2]\cdot 2H_2O$ while in a study of the thermal decomposition of this salt the authors [4] assign only one molecule of water to this compound. In another thermoanalytical work [5], the authors found the existence of two water molecules.

The potassium oxalato titanate(IV) crystallizes in a tricinlic unit cell. The observed and calculated densities agree well if the unit cell contains 4 $\{K_2[TiO(C_2O_4)_2]\cdot 2H_2O\}$ formulae. The structural investigation of this compound [6] recently undertaken indicates the existence of a tetrameric anion having

TABLE II. Observed and Calculated d-Spacings (Å) and Observed Relative Intensities for $M_2[TiO(C_2O_4)_2]\cdot nH_2O$ Complexes.

Li				Na				K				Rb				Cs			
hkl	d_o	d_c	I/I_o	hkl	d_o	d_c	I/I_o	hkl	d_o	d_c	I/I_o	hkl	d_o	d_c	I/I_o	hkl	d_o	d_c	I/I_o
110	10.16	10.09	60	001	10.6	10.5	90	010	10.07	10.05	70	001	11.0	10.9	75	001	11.7	11.1	50
011	9.21	9.16	100	100	8.98	8.81	100	011	9.02	9.41	70	011	8.97	9.11	45	011	9.69	9.57	50
020	7.14	7.13	60	012	5.67	6.66	20	110	7.81	7.80	80	11$\bar{1}$	6.00	5.83	20	012	5.93	5.87	10
002	6.01	5.98	40	020	4.968	4.951	20	111	7.48	7.45	20	102	4.816	4.811	50	121	5.51	5.52	30
121	5.617	5.629	20	10$\bar{2}$	4.495	4.490	40	101	7.12	7.18	80	120	4.181	4.185	35	120	5.18	5.20	20
112	5.148	5.144	30	210	4.348	4.339	5	0$\bar{1}$1	6.32	6.25	5	11$\bar{2}$	4.025	4.049	35	102	4.848	4.875	40
031	4.423	4.419	80	211	4.281	4.300	5	012	5.789	5.798	10	222	3.818	3.824	45	201	4.688	4.714	40
222	3.854	3.855	25	$\bar{1}$22	3.818	3.824	60	121	5.231	5.240	5	031	3.623	3.611	20	0$\bar{1}$2	4.295	4.304	20
032	3.735	3.722	25	013		3.811		1$\bar{1}$1	4.976	4.965	75	21$\bar{2}$	3.415	3.408	100	222	3.917	3.937	20
040	3.569	3.566	70	212	3.689	3.687	70	102	4.695	4.703	75	$\bar{2}$21	3.281	3.295	50	202	3.789	3.783	50
0.41	3.420	3.417	20	023	3.615	3.616	30	$\bar{2}$10	4.058	4.056	15	320	3.168	3.179	100	132	3.688	3.688	50
141	3.324	3.324	20	113		3.610		013	3.913	3.914	15	322	3.040	3.047	10	030	3.506	3.507	100
240	3.189	3.190	10	132	3.510	3.500	40	222	3.731	3.726	5	20$\bar{3}$	2.930	2.934	10	10$\bar{3}$		3.505	
042	3.074	3.063	30	003		3.499		003	3.601	3.608	50	32$\bar{1}$	2.880	2.887	25	$\bar{2}$21	3.446	3.447	100
133	2.988	2.987	15	202	3.395	3.396	5	1$\bar{2}$1	3.503	3.502	50	312	2.757	2.767	30	$\bar{2}$22	3.237	3.235	50
114	2.864	2.867	20	$\bar{1}$13		3.393		300	3.229	3.229	10	041	2.687	2.694	30	$\bar{3}$11	3.094	3.095	20
150	2.782	2.798	35	310	2.972	2.972	15	0$\bar{2}$2	3.129	3.126	20	410	2.603	2.605	20	004	2.771	2.774	50
342	2.580	2.575	10	230	2.917	2.917	20	320	3.003	3.006	100	421	2.543	2.549	20	411	2.659	2.664	20
152	2.537	2.534	10	$\bar{1}$30		2.917		113	2.954	2.961	10	41$\bar{1}$	2.481	2.480	20	30$\bar{3}$	2.558	2.560	10
243	2.491	2.491	5	0$\bar{3}$1	2.853	2.842	15	20$\bar{3}$	2.903	2.908	100	430	2.306	2.306	10	40$\bar{1}$		2.560	
343	2.322	2.320	30	124	2.805	2.795	15	141	2.745	2.746	5	250	2.070	2.069	10	$\bar{2}$33	2.516	2.517	10
071	2.012	2.009	20	141	2.708	2.701	40	31$\bar{2}$	2.671	2.667	5					422		2.515	
080	1.786	1.783	15	302	2.576	2.575	5	10$\bar{4}$	2.618	2.613	15					1$\bar{3}$2	2.398	2.403	20
562	1.747	1.747	10					234	2.506	2.505	10					432		2.396	
								303	2.394	2.394	5					015	2.348	2.351	80
								412	2.322	2.323	5					41$\bar{2}$		2.351	
								$\bar{3}$14	2.114	2.114	10					413	2.262	2.262	20
								$\bar{2}$15	2.057	2.056	5					$\bar{2}$34		2.262	
								414	1.906	1.907	15					$\bar{2}$42		2.262	
																441	2.192	2.193	20
																41$\bar{2}$	2.139	2.142	10
																511		2.138	
																41$\bar{3}$	2.101	2.100	10
																0$\bar{4}$2		2.099	
																1$\bar{3}$3	2.071	2.073	10
																530	2.014	2.014	10

TABLE IV. Observed IR Vibration Frequencies (cm^{-1}) for the Alkaline Salts of $M_2[TiO(C_2O_4)_2]\cdot nH_2O$.[a]

Li	Na	K	NH_4	Rb	Cs	$K_3[Cr(C_2O_4)_3]\cdot 3H_2O$		
						Frequency	Assignment (7)	(Fig. 1)
1710 vs	1710 vs	1710 vs	1708 vs	1708 vs	1705 vs	1708 vs	$\nu_{as}(C{=}O)$ ν_7	
1678 vs 1640 sh	1678 vs 1642 sh	1680 vs 1650 sh	1675 vs 1625 sh	1680 vs 1625 sh	1670 vs 1625 sh	1680 vs 1640 vs	$\nu_{as}(C{=}O)$ ν_1	A
1395 s	1385 s	1378 s	1389 vs	1375 s	1392 s	1388 vs	$\nu_s(C–O)$ ν_2 $+ \nu(C–C)$	B
1251 m	1241 w	1235 m	1235 m	1232 m	1230 m	1254 m	$\nu_s(C–O)$ ν_8 $+ \delta(O–C{=}O)$	C
910, 892 w	888 w	894 w	885 w	888 w	885 w	895 w	$\nu_s(C–O)$ ν_3 $+ \delta(O–C{=}O)$	D
799 s	795 s 770 sh	788 vs 769 sh	770 vs 750 s	785 s 747 sh	785 s 760 sh	811 m 799 sh	$\delta(O–C{=}O)$ ν_9 $+ \nu(M–O)$	E
625 w	630–685 w	620 w	575			598 w	Water of crystallisation?	
515 m	512 m	515 m	515 m	512 m	510 m	545 m	$\nu(M–O)$ $+ \nu(C–C)$ ν_4	
492, 460	490, 458 w	496, 462 w	460 w	462 m	460 w	485 m	Cycle deformation $+ \delta(O–C{=}O)$ ν_{10}	
392 w	392 sh	388 m	395 m	395 m	391 w	415 s	Cycle deformation $+ \nu(M–O)$ ν_{11}	
372 w	372 w	365 sh	340 sh	340 sh	360 sh	358 sh	$\delta(O–C{=}O)$ ν_5	
290	295 m	300 m	290	295 m	295 m	310 w	π	

[a] vs, very strong; s, strong; m, medium; w, weak; sh, shoulder.

a center of symmetry. The study also reveals that some of the water molecules are disordered, and amount to between 1 and 2 molecules per $\{K_2[TiO(C_2O_4)_2]\}$ group.

$Na_2[TiO(C_2O_4)_2]\cdot 3H_2O$, $Rb_2[TiO(C_2O_4)_2]\cdot H_2O$ and $Cs_2[TiO(C_2O_4)_2]\cdot H_2O$

As shown in Table II, the powder diffraction films of these three compounds could be indexed using triclinic unit cells similar in dimensions to that of the potassium salt. The observed and calculated densities for the Cs salt are in very good agreement when the unit cell content is taken as $4\{Cs_2[TiO(C_2O_4)_2]\cdot H_2O\}$. Except for the lithium salt which crystallizes in the tetragonal system, all the other alkaline oxalato titanate(IV) complexes have a triclinic unit cell. The volume of the unit cells increases regularly with the size of the cation. Although the water content is not constant for these compounds, it seems, nonetheless, that they are isostructural. The four alkaline oxalato titanate(IV) complexes would be constituted of centrosymmetric tetrameric anions. It is possible that the packing of these large anions leaves enough empty space to accommodate the cations and a variable number of water molecules. It should be pointed out that the number of water molecules decreases while the size of the cation increases.

Infrared Spectra

The IR spectra of the alkaline salts of the oxalato titanate(IV) complexes are presented in Figure 1 (Table IV). Except for the region beyond 2500 cm^{-1}, corresponding to H_2O and NH_4^+ vibrations, these spectra and that of potassium trisoxalato chromate(III) show a very strong resemblance. For this reason, the IR spectrum of $K_3[Cr(C_2O_4)_3]\cdot 3H_2O$ has been included in Figure 1.

The vibration frequencies of potassium trisoxalato chromate(III) have been assigned [7] and are compar-

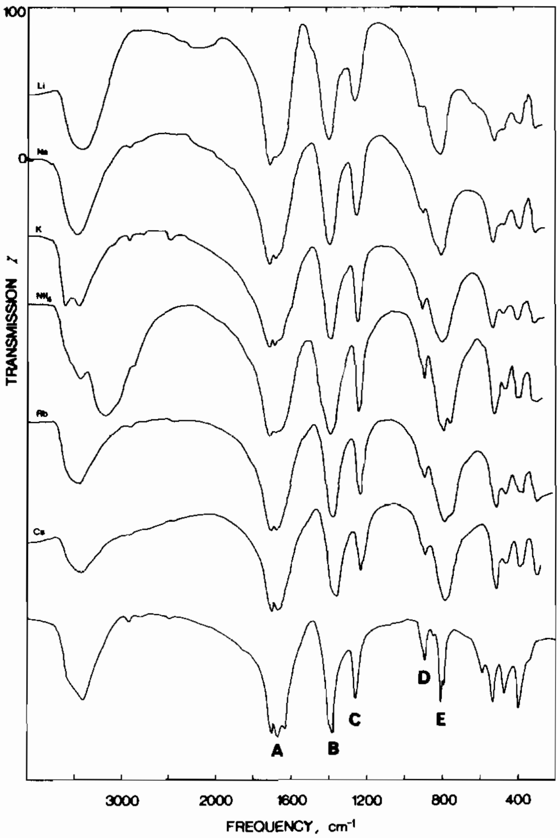

Figure 1. Infrared spectra of the oxalato titanate(IV) complexes, $M_2[TiO(C_2O_4)_2]\cdot nH_2O$, where M = Li, Na, K, Rb and Cs. The lowest spectrum is that of $K_3[Cr(C_2O_4)_3]\cdot 3H_2O$.

ed in Table IV with the vibration frequencies of the alkaline salts of the oxalato titanate(IV) complexes. The bands referred to by A, B, C and D on Figure 1 are practically unchanged from $K_3[Cr(C_2O_4)_3]\cdot 3H_2O$ to $M_2[TiO(C_2O_4)_2]\cdot nH_2O$. This is not too surprising since these bands have been assigned to vibrations of the oxalato group alone. However, band E, which is a narrow doublet for the trisoxalato chromate(III), is wider in the case of the oxalato titanate(IV) complexes. According to Fujita [7] this doublet is a combination $\delta(O\text{–}C{=}O) + \nu(M\text{–}O)$. Finally, the ν_4 (545 cm^{-1}) and ν_{11} (415 cm^{-1}) bands in the trisoxalato chromate(III) would correspond to the bands at 515 and 390 cm^{-1} in $M_2[TiO(C_2O_4)_2]\cdot nH_2O$. These two bands are also combinations where the $\nu(M\text{–}O)$ contribution dominates. The shift in the ν_4 and ν_{11} frequencies could be due to the fact that Cr is replaced by the lighter Ti atom and also to the fact that the 3 Cr–O bonds, whose lengths average [8] 1.90Å, are shorter than the 6 Ti–O bonds which have an average length of 1.97Å.

The lowering of the frequencies could be attributed as well to the existence of the cyclic system of 4 connected octahedra forming the tetrameric anion $[TiO(C_2O_4)_2]_4^{8-}$ while in potassium trisoxalato chromate(III), the anions are constituted of individual octahedra.

Acknowledgments

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