December, 1979] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (12), 3697—3701 (1979) 3697

New Potassium and Ammonium Lead(II) Chromates with a Higher Lead Content and Iso-structural with Potassium Lead(II) Chromate, $K_2Pb(CrO_4)_2$

Tsutomu Fukasawa* and Masaaki Iwatsuki

Department of Applied Chemistry, Faculty of Engineering, Yamanashi University, Takeda, Kofu 400

(Received April 16, 1979)

An unknown yellow precipitate, similar to lead(II) chromate in appearance, has been reported. The precipitate was formed in the detection process of lead(II) ions using chromate ions by a classical qualitative analytical method. The present paper describes the elucidation of the unknown precipitate, and the presence of a series of new chromates iso-structural with the known potassium lead(II) chromate, $K_2Pb(CrO_4)_2$. The new chromates are explained as new stoichiometric chromates, $K_4Pb_4(CrO_4)_6$ and $(NH_4)_4Pb_4(CrO_4)_6$ [$=K_2Pb_2(CrO_4)_3$ and $(NH_4)_2Pb_2(CrO_4)_3$], and solid solutions $(K, NH_4)_{6-2z}Pb_{3+z}(CrO_4)_6$ ($z=+0.3$—$+1.2$) among the new stoichiometric chromates and the known chromates, $K_6Pb_3(CrO_4)_6$ and $(NH_4)_6Pb_3(CrO_4)_6$ [$=K_2Pb(CrO_4)_2$ and $(NH_4)_2Pb(CrO_4)_2$]. The compositions of the new chromates are dependant on the precipitating conditions. Relationships between compositions, lattice constants, and precipitating conditions are given together with indexed powder diffraction data for references to identification, and the results of thermal analyses.

It was described in a previous paper[1] that fine particles of an unknown yellow compound, similar to lead(II) chromate in appearance, precipitated under certain conditions in the reaction leading to the formation of lead(II) chromate, a substance used for the detection of lead(II) ions in classical qualitative analysis. The particles were unstable and changed into needle crystals of monoclinic lead(II) chromate when left in the mother liquor. In general, this unknown compound precipitated when a potassium chromate solution was added to a hot and dilute lead(II) solution containing a relatively large amount of ammonium acetate.

The present study was conducted to elucidate the unknown compound, and to obtain the powder X-ray diffraction data for identification. Precipitates were prepared by adding an ammonium chromate solution to an ammonium acetate solution of lead(II), or a potassium chromate solution to a potassium acetate solution of lead(II) at different concentrations and pH. X-Ray diffraction, chemical analysis, density measurement, and thermal analysis were conducted on the precipitates.

It was found that the unknown compound described was one of a series of new chromates, which were higher in lead content than the known potassium or ammonium lead(II) chromate $K_2Pb(CrO_4)_2$ or $(NH_4)_2Pb(CrO_4)_2$,[2] and iso-structural with known chromates. These new chromates have been expressed as $K_2Pb_2(CrO_4)_3$, $(NH_4)_2Pb_2(CrO_4)_3$, and $(K,NH_4)_{2+2y}Pb_{2-y}(CrO_4)_3$ ($y=-0.1$—$+0.3$) from the construction rule of chemical formulas and the analytical results, and as $(K,NH_4)_{2-2x}Pb_{1+x}(CrO_4)_2$ ($x=+0.1$—$+0.4$) when the conventional formula of the known chromate, $K_2Pb(CrO_4)_2$, was followed. The relationship between the new and known stoichiometric chromates is conveniently explained by the common formulas containing six chromate ions from the viewpoint of iso-structure: The new chromate are explained as new stoichiometric chromates, $K_4Pb_4(CrO_4)_6$ and $(NH_4)_4Pb_4(CrO_4)_6$, and solid solutions, $(K,NH_4)_{6-2z}Pb_{3+z}(CrO_4)_6$ ($z=+0.3$—$+1.2$), among the new stoichiometric chromates and the known chromates, $K_6Pb_3(CrO_4)_6$ and $(NH_4)_6Pb_3(CrO_4)_6$. The relationships between the compositions, lattice constants, and precipitating conditions of the new chromates are given with the indexed powder X-ray diffraction data, and the results of thermal analyses.

Experimental

Sample Preparation. Several differing lead(II) acetate solutions were prepared by the dissolution of appropriate quantities of lead(II) sulfate in ammonium or potassium acetate solutions of 1 to 6 M (1 M$=$1 mol dm^{-3}), followed by pH adjustment. The precipitates were prepared using each lead(II) acetate solution as follows: A small excess of a 1.5 M ammonium or potassium chromate solution was gradually added *via* a 5 cm^3 pipet to a lead(II) acetate solution in a 200 cm^3 or 1 dm^3 beaker at about 80 °C with stirring. The precipitate formed was filtered off, and dried at 105 °C in an electric oven.

All the precipitates prepared were yellow or yellow-orange, and fine particles smaller than 1 μm except that monoclinic lead(II) chromate occasionally precipitated in size of above 1 μm.

The precipitate samples used for the chemical analyses were identified by powder X-ray diffraction analysis.

Methods of Analysis. *Powder X-Ray Diffraction Analysis*: The X-ray diffraction analyses were conducted by use of an X-ray diffractometer (Rigaku) equipped with a copper-target tube and nickel filter. The sample was mounted in a standard aluminum specimen holder. The intensities were measured from the peak heights of the line profiles. The accurate diffraction angle for determination of the lattice constants was measured from the center of gravity of the line profile recorded at a low scanning speed. The diffraction angle was corrected by use of high-purity silicon powder as an internal standard.

Chemical Analysis: X-Ray fluorescence analysis and Nessler's test confirmed that the samples contained lead, chromium, potassium, and/or ammonium, but no sulfur. Lead, chromium, potassium, and ammonium were quantitatively determined as follows: For the determination of lead and potassium, the sample was dissolved in nitric acid (1+1), followed by dilution with water. Ascorbic acid was then added to reduce the chromate to chromium(III) ions. After an appropriate dilution, lead and potassium were determined by the standard addition-atomic absorption method and by the standard addition-flame photometric method, respectively. For the determination of chromium, the sample was dissolved in nitric acid (1+1), and sodium hydroxide solution added until the solution became alkaline. The chromate ion was photometrically determined at 366 nm. The ammonium ion was determined by the micro-diffusion method.[3] The determination of each constituent was repeated at least twice and the average taken.

Density: "Observed density" was determined by use of a pycnometer with carbon tetrachloride. "Calculated density" was evaluated from lattice constants and the number of constituent ions in a unit cell.

Thermal Analysis: Thermal analysis was conducted by use of a thermobalance (Rigaku) with a differential thermal analyzer.

Results and Discussion

Chemical Composition and Crystallographic Consideration. Table 1 shows the results of chemical analyses of the representative samples prepared under different conditions, and chemical formulas obtained from the analytical results. The number of oxygens in the chemical formulas has been taken as 12, because the elemental ratio in the formula of sample K-0 was successfully expressed in the smallest integer when the conventional rule was applied to the construction of chemical formulas; the ratios in the formulas of the other samples were not successfully expressed in integers.

The lead contents of the prepared samples were higher than those of the known chromates, $K_2Pb(CrO_4)_2$ and $(NH_4)_2Pb(CrO_4)_2$. The chemical formulas of some samples were approximated to $K_2Pb_2(CrO_4)_3$ or $(NH_4)_2Pb_2(CrO_4)_3$. The other samples were nonstoichiometric, and have been expressed as $(K,NH_4)_{2+2y}Pb_{2-y}(CrO_4)_3$ ($y=-0.1$—$+0.3$). Some however have a slightly unbalanced charge. The charge unbalance in some formulas may be explained by the formation of nonstoichiometric compounds of lattice-defect type, and/or the presence of undetectable amounts of lead oxide which may be formed by heating lead hydroxide at 105 °C; the lead hydroxide may be produced together with the chromate in the precipitating process.

The X-ray powder patterns of the newly found chromates were similar to those of the known chromates (hexagonal), $K_2Pb(CrO_4)_2$, $(NH_4)_2Pb(CrO_4)_2$, *etc.*, and indexed successfully by the hexagonal system by use of the Bunn-Bjurström chart. Table 2 shows the X-ray diffraction data of the representative samples. It appears that the crystal structures of all the newly found chromates are iso-structural with the known chromates. The compounds previously expressed as $K_2Pb_2(CrO_4)_3$, $(NH_4)_2Pb_2(CrO_4)_3$, and $(K,NH_4)_{2+2y}Pb_{2-y}(CrO_4)_3$ may be expressed as $K_{1.33}Pb_{1.33}(CrO_4)_2$, $(NH_4)_{1.33}Pb_{1.33}(CrO_4)_2$, and $(K,NH_4)_{2-2x}Pb_{1+x}(CrO_4)_2$ assuming the conventional formulas of the known chromates are followed. The formulas $K_{1.33}Pb_{1.33}(CrO_4)_2$ and $(NH_4)_{1.33}Pb_{1.33}(CrO_4)_2$ do not however adhere to the construction rule of chemical formulas. The common formulas containing six chromate ions (oxygen=24) appear to fit both the new and known chromates which are stoichiometric and iso-structural with each other. The chromates $K_2Pb_2(CrO_4)_3$ and $(NH_4)_2Pb_2(CrO_4)_3$ are explained conveniently as the new stoichiometric chromates $K_4Pb_4(CrO_4)_6$ and $(NH_4)_4Pb_4(CrO_4)_6$ iso-structural with the known chromates $K_6Pb_3(CrO_4)_6$ and $(NH_4)_6Pb_3(CrO_4)_6$. The nonstoichiometric chromates expressed by $(K,NH_4)_{2+2y}Pb_{2-y}(CrO_4)_3$ are thought to be substitutional solid solutions lying between the new and known stoichiometric chromates, and are expressed by the general formula, $(K,NH_4)_{6-2z}Pb_{3+z}(CrO_4)_6$ ($z=+0.3$—$+1.2$). The latter formulas will be used in the subsequent discussion except for the thermal analysis.

Tables 3 and 4 show the precipitating conditions, lattice constants, chemical formulas, and densities of the representative compounds prepared; the lattice constants were calculated from accurate diffraction angles of appropriate lines and their assigned indices. The compositions of the compounds changed depending on the precipitating conditions; such changes were also supported by the differences in lattice constants. The relationships between the compounds formed and the precipitating conditions may be summarized as follows: (1) the lead content of the formed compound increased with decreasing concentration of ammonium or potassium acetate solution; (2) the lattice constant, *a*, of the compound increased with increasing lead content, while the lattice constant, *c*, decreased except in compounds obtained with potassium acetate solution; (3) monoclinic lead(II) chromate was preferentially formed when ammonium or potassium acetate solution of lower concentration was used; (4) the pH, and amounts of ammonium or potassium acetate solution per gram of lead(II) sulfate do not appear to affect the composition.

The number of chemical units in the unit cell, which was calculated from the observed density and lattice constants, was one for a series of the new chromates, $(K,NH_4)_{6-2z}Pb_{3+z}(CrO_4)_6$, as well as for the known chromates, $K_6Pb_3(CrO_4)_6$ and $(NH_4)_6Pb_3(CrO_4)_6$.

TABLE 1. RESULTS OF CHEMICAL ANALYSES AND CHEMICAL FORMULAS OF THE REPRESENTATIVE SAMPLES

Sample	wt%					Chemical formula (O=12)	Unbalance of charge
	K^+	NH_4^+	Pb^{2+}	CrO_4^{2-}	Sum		
NK-0	1.0	4.6	52	45	102	$K_{0.2}(NH_4)_{2.0}Pb_{1.9}(CrO_4)_{3.0}$	±0.0
N-0	—	5.7	51	44	101	$(NH_4)_{2.4}Pb_{1.9}(CrO_4)_{3.0}$	+0.2
N-5	—	5.9	46	47	99	$(NH_4)_{2.5}Pb_{1.7}(CrO_4)_{3.0}$	−0.1
N-15	—	3.9	54	42	100	$(NH_4)_{1.8}Pb_{2.1}(CrO_4)_{3.0}$	±0.0
K-0	9	—	49	41	99	$K_{2.0}Pb_{2.0}(CrO_4)_{3.0}$	±0.0
K-8	13	—	46	42	101	$K_{2.7}Pb_{1.8}(CrO_4)_{3.0}$	+0.3

Table 2. Powder X-ray diffraction data for the representative prepared samples, $(NH_4)_2Pb(CrO_4)_2$, and $K_2Pb(CrO_4)_2$[a)]

hkl[b)]	Sample NK-0 $K_{0.2}(NH_4)_{2.0}Pb_{1.9}(CrO_4)_{3.0}$			Sample N-0 $(NH_4)_{2.4}Pb_{1.9}(CrO_4)_{3.0}$			Sample K-0 $K_{2.0}Pb_{2.0}(CrO_4)_{3.0}$			JCPDS card No. 19-66 $(NH_4)_2Pb(CrO_4)_2$		JCPDS card No. 19-971 $K_2Pb(CrO_4)_2$	
	d_{calcd}/Å	d_{obsd}/Å	I_{obsd}	d_{calcd}/Å	d_{obsd}/Å	I_{obsd}	d_{calcd}/Å	d_{obsd}/Å	I_{obsd}	d/Å	I/I_1	d/Å	I/I_1
003	7.241	7.30	34	7.240	7.28	61	7.010	N.D.	—	7.30	10	7.02	8
101	4.889	4.91	17	4.890	4.90	16	4.844	4.85	13	4.88	6	4.82	5
012	4.554	4.57	60	4.556	4.55	65	4.499	4.50	12	4.54	35	4.48	18
104	3.685	3.69	2	3.686	3.69	3	3.615	3.61	1	N.D.	—	3.609	3
006	3.620	N.D.	—	3.620	N.D.	—	3.505	3.51	3	N.D.	—	3.512	3
015	3.284	3.29	100	3.285	3.29	100	3.213	3.21	100	3.30	95	3.208	100
110	2.896	2.90_1	70	2.898	2.89_4	61	2.874	2.87_5	53	2.885	95	2.858	79
113	2.689	2.68_6	47	2.690	2.69_1	43	2.659	2.65_9	13	2.684	80	2.646	24
107	2.639	2.64_1	13	2.639	2.64_4	13	2.572	2.57_3	5	2.653	20	2.571	11
021	2.492	2.49_2	2	2.493	2.49_1	2	2.472	N.D.	—	2.483	10	2.459	8
202	2.444	2.44_5	3	2.445	2.44_2	2	2.422	2.42_2	1	2.436	10	N.D.	—
009	2.414	2.41_7	2	2.413	2.41_5	2	2.337	2.33_5	2			2.349	20
018	2.388	2.39_1	3	2.388	2.39_2	3	2.325	N.D.	—	2.402	16	N.D.	—
024	2.277	2.27_8	15	2.278	2.27_6	10	2.250	2.25_1	10	2.270	85	2.240	26
116	2.262	2.26_2	15	2.262	2.26_5	14	2.222	2.22_2	8			2.217	20
205	2.172	2.17_3	22	2.173	2.17_1	21	2.142	2.14_0	16	2.172	70	2.134	60
10$\underline{10}$	1.993	1.994	13	1.993	1.997	14	1.937	1.937	17	2.008	60	1.938	61
027	1.951	1.952	2	1.951	1.953	2	1.917	N.D.	—	1.954	16	N.D.	—
211	1.889	1.889	4	1.890	1.888	3	1.874	1.875	2	1.882	16	N.D.	—
122	1.868	1.868	9	1.869	1.866	8	1.852	1.853	2	N.D.	—	N.D.	—
119	1.854	N.D.	—	1.854	N.D.	—	1.813	1.810	4	1.861	80	1.808	16
208	1.843	1.842	9	1.843	1.843	8	1.807			1.848	60		
01$\underline{11}$	1.838			1.837			1.785	1.785	1			N.D.	—
00$\underline{12}$	1.810	1.810	1	1.810	1.814	2	1.753	1.754	1	1.827	16	1.756	12
125	1.738	1.738	14	71.39	1.737	11	1.717	1.717	9	1.735	80	1.710	72
300	1.672	1.672	6	1.673	1.670	5	1.659	1.659	4	1.666	45	1.650	30
02$\underline{10}$	1.642	1.642	4	1.642	1.642	3	1.606			1.648	30	1.605	39
303	1.629	1.629	7	1.630	1.626	5	1.615	1.606 (Broad)	5	1.621 (Broad)	70		
217	1.618	1.618	5	1.619	1.621	3	1.595					N.D.	—
10$\underline{13}$	1.585	1.584	2	1.585	1.590	1	1.539	N.D.	—	1.598	20	N.D.	—
128	1.555	1.554	3	1.555	1.555	2	1.530	N.D.	—	1.557	30	N.D.	—
20$\underline{11}$	1.552			1.552			1.516	N.D.	—			N.D.	—
11$\underline{12}$	1.535	1.535	2	1.535	1.537	2	1.496	1.498	1	1.544	30	1.495	20
306	1.518	N.D.	—	1.519	N.D.	—	1.500			N.D.	—		
220	1.448	1.447	6	1.449	1.447	4	1.437	1.437	3	1.443	60	1.429	58
00$\underline{15}$	1.448			1.448			1.402	1.402	5	1.461	30	1.401	74
21$\underline{10}$	1.428	1.427	6	1.429	1.429	6	1.402			1.431	100		
309	1.375	1.378	2	1.375	1.378	2	1.353	1.353	1	1.375	35	N.D.	—
315	1.325	1.325	3	1.326	1.324	3	1.312	1.311	1	1.322	70	1.305	35
11$\underline{15}$	1.295	1.294	2	1.295	1.297	2	1.260	1.260	3	1.304	60	1.260	36

a) N.D.: Not detected. d_{calcd} was calculated with lattice constants measured in this work. b) Miller's indices are shown as one of hexagonal lattice.

Comparison of the lattice constants in Table 3 appears to indicate that the substitution of one Pb^{2+} ion for two NH_4^+ ions causes a slight decrease in c, and a slight increase in a, but no appreciable change in the volume of the unit cell. The Table 4 shows that the substitution of one Pb^{2+} ion for two K^+ ions has little effect on c, but causes a slight increase in a. In terms of the differences in number and size of the cations in their unit cells, the newly found chromates appear to be less compact in structure than the known chromates. The instability of the new chromates in their mother liquors may be explained by the less compact structures.

Thermal Analysis. Figure 1 shows the results of thermogravimetric (TGA) and differential thermal (DTA) analyses of sample NK-0. The endothermic

TABLE 3. PRECIPITATING CONDITIONS, LATTICE CONSTANTS, CHEMICAL FORMULAS, AND DENSITIES OF THE COMPOUNDS FORMED USING AMMONIUM ACETATE SOLUTIONS[a)]

Sample	Lead acetate soln.			NH_4^+/Pb^+ mole ratio	pH	Lattice constants/Å		Chemical formula (O=24)	Density g/cm³	
	$PbSO_4$	NH_4OAc								
	g	Concn M	Amount cm³	10^2		*a*	*c*		Obsd	Calcd
NK-0	1.00	*ca.*4	100	*ca.*1.2	6—7	5.793	21.72	$K_{0.4}(NH_4)_{4.0}Pb_{3.8}(CrO_4)_{6.0}$	4.05	4.133
N-0	0.20	*ca.*4	18	*ca.*1.1	6—7	5.796	21.72	$(NH_4)_{4.8}Pb_{3.8}(CrO_4)_{6.0}$	4.26	4.062
N-1	1.00	6	25	0.45	7.0	5.784	21.80			
N-2	1.00	6	50	0.90	7.1	5.785	21.80			
N-3	1.00	6	100	1.8	7.0	5.785	21.83			
N-4	1.00	6	200	3.6	7.0	5.783	21.84			
N-5	1.00	6	400	7.2	7.1	5.781	21.85	$(NH_4)_{5.0}Pb_{3.4}(CrO_4)_{6.0}$		
N-14[b)]	1.00	3	200	1.8	7.2	5.792	21.61			
N-15	1.00	3	400	3.6	7.2	5.791	21.62	$(NH_4)_{3.6}Pb_{4.2}(CrO_4)_{6.0}$		
N-13[c)]	1.00	2	400	2.4	7.3	—	—			
d)						5.777	21.939	$(NH_4)_6Pb_3(CrO_4)_6$ $[=(NH_4)_2Pb(CrO_4)_2]$	3.71	3.734

a) A given amount of $PbSO_4$ was dissolved in a hot solution of NH_4OAc, and 1.5 M $(NH_4)_2$ CrO_4 (1.5 M K_2CrO_4 for NK-0) was added. b) A trace amount of $PbCrO_4$ (mon.) was detected. c) A large amount of $PbCrO_4$(mon.) was detected. d) JCPDS card No. 19-66 and Ref. 2.

TABLE 4. PRECIPITATING CONDITIONS, LATTICE CONSTANTS, CHEMICAL FORMULAS, AND DENSITIES OF THE COMPOUNDS FORMED USING POTASSIUM ACETATE SOLUTIONS[a)]

Sample	Lead acetate soln.			K^+/Pb^{2+} mole ratio	Added amount of concd HOAc	pH	Lattice constants/Å		Chemical formula (O=24)	Density g/cm³	
	$PbSO_4$	KOAc									
	g	Concn M	Amount cm³	10^2	cm³		*a*	*c*		Obsd	Calcd
K-0	0.60	*ca.*3	75	*ca.*1.1	0	6—7	5.748	21.03	$K_{4.0}Pb_{4.0}(CrO_4)_{6.0}$	4.76	4.639
K-1	1.00	4	150	1.8	0	8.9	5.729	21.04			
K-4	1.00	4	150	1.8	1.0	7.5	5.728	21.04			
K-5	1.00	4	150	1.8	3.0	6.6	5.728	21.02			
K-6	1.00	4	150	1.8	10.0	5.9	5.727	21.03			
K-8	1.00	4	125	1.5	0	8.8	5.730	21.04	$K_{5.4}Pb_{3.6}(CrO_4)_{6.0}$		
K-7	1.00	3	125	1.1	0	8.4	5.742	21.06			
K-9	1.00	2	125	0.8	0	8.1	5.751	21.07			
K-11[b)]	1.00	1	125	0.4	0	7.7	—	—			
K-2	1.00	4	300	3.6	0	8.9	5.736	21.03			
K-3	1.00	4	600	7.2	0	8.8	5.740	21.03			
c)							5.716	21.065	$K_6Pb_3(CrO_4)_6$ $[=K_2Pb(CrO_4)_2]$	4.30	4.324

a) A given amount of $PbSO_4$ was dissolved in a hot solution of KOAc, HOAc was added if required, and 1.5 M K_2CrO_4 was added. b) A large amount of $PbCrO_4$ (mon.) and a small amount of Pb_2 $(OH)_2CrO_4$ were detected. c) JCPDS card No. 19-971 and Ref. 2.

peak at approximately 205 °C, which was accompanied by a weight loss over the range 140 to 220 °C, was attributed to the evolution of ammonia; the evolution was confirmed by Nessler's test and the experimental and theoretical weight losses. The exothermic peak at approximately 245 °C, which was accompanied by a weight loss over the range 220 to 270 °C, may be attributable to the formation of water by the oxidation of ammonia, since, when the sample was heated to approximately 220 °C in a test tube attached with a conduit pipe, water drops were produced inside the pipe. High-temperature X-ray diffraction analysis showed a definite transition of sample NK-0 to monoclinic lead(II) chromate and the formation of an intermediate compound in the couse of this transition. Although this intermediate compound could not be identified, it appears to be a compound formed by the escape of ammonia from sample NK-0. The exothermic peak free from weight loss at approximately 405 °C appears due to a crystal transition. The transition could not, however, be detected by high-temperature X-ray diffraction analysis.

Several samples changed to known compounds with weight loss, when heated up to approximately 400 °C in an electric furnace, the results of which are summarized in Table 5. The residues obtained by heating

Table 5. The results of heating to 400 °C for some samples

Sample	Weight loss/%	Color of the residue	Crystalline phase in the residue	
			Major component	Minor component
NK-0	9	Yellow-green	$PbCrO_4$(mon.)	$K_2Pb(CrO_4)_2$
N-0	12	Yellow-green	$PbCrO_4$(mon.)	—
K-0	0.7	Orange	$K_2Pb(CrO_4)_2$	$PbCrO_4$(mon.), $PbCrO_4 \cdot PbO$

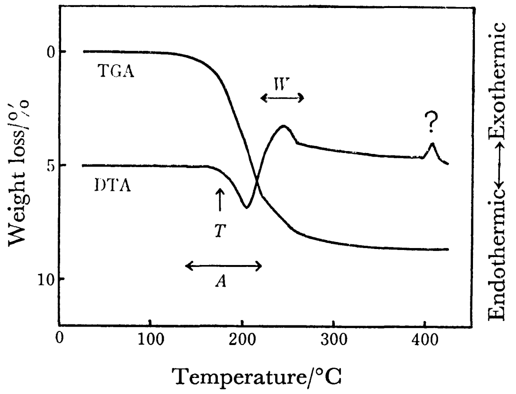

Fig. 1. Thermal analysis of $K_{0.2}(NH_4)_{2.0})Pb_{1.9}(CrO_4)_{3.0}$ (sample NK-0).
Heating rate: 3 °C/min; T: transition of sample NK-0 to $PbCrO_4$ (mon.); A: evolution of ammonia; W: evolution of water.

samples NK-0 and N-0 mainly consisted of monoclinic lead(II) chromate; small amounts of the known chromate, $K_2Pb(CrO_4)_2$, were also detected in the residue of sample NK-0 containing small amounts of potassium ions. Amorphous chromium(III) oxide appears to be present in both residues judging from the color (yellow-green). This chromium(III) oxide may be formed by the reduction of chromate ions by ammonia. Sample K-0 was decomposed by heat-treatment to known compounds, $K_2Pb(CrO_4)_2$, $PbCrO$(mon.), $PbCrO_4 \cdot PbO$, *etc.*

The thermal analyses described above, together with the differences in X-ray diffraction patterns and lattice constants, also support the conclution that the compounds prepared here differ from the known chromates, $K_2Pb(CrO_4)_2$ and $(NH_4)_2Pb(CrO_4)_2$.

The authors are grateful to Professor Yoshihiko Saito of the University of Tokyo, Professor G. H. Morrison of Cornell University, and Dr. L. S. Birks of the Naval Research Laboratory for their advice. Acknowledgments are also due to Mr. Jun'ichi Ito of the Central Research Laboratory, Showa Denko K. K., for providing the facilities for thermal analysis, to Rigaku Denki K. K. for providing the facilities for high-temperature X-ray diffraction analysis, and to Mr. Shintaro Suzuki for assistance in the experimental work.

References

1) T. Fukasawa and M. Iwatsuki, *Bunseki Kagaku*, **26**, 379 (1977).
2) H. Schwarz, *Z. Anorg. Allg. Chem.*, **345**, 230 (1966).
3) K. Saruhashi, *Bunseki Kagaku*, **4**, 337 (1955).