

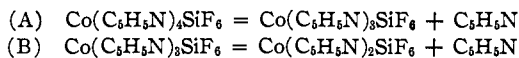
The thermal dissociation of cadmium tetrapyrindine fluosilicate gave a pressure of approximately 4 mm. at 77°, but there was also a slow evolution of silicon tetrafluoride with the formation of a sublimation product of pyridine and silicon tetrafluoride. This system, therefore, was not investigated further. In the cases of copper, nickel and zinc, the dissociation pressures were even lower than with the cadmium compound.

### Summary

Five new complex salts of fluosilicic acid have been prepared from solution and have been described. These are

Cupric tetrapyrindine fluosilicate monohydrate	$\text{Cu}(\text{C}_5\text{H}_5\text{N})_4\text{SiF}_6 \cdot \text{H}_2\text{O}$
Cobalt tetrapyrindine fluosilicate	$\text{Co}(\text{C}_5\text{H}_5\text{N})_4\text{SiF}_6$
Nickel tetrapyrindine fluosilicate	$\text{Ni}(\text{C}_5\text{H}_5\text{N})_4\text{SiF}_6$
Zinc tetrapyrindine fluosilicate	$\text{Zn}(\text{C}_5\text{H}_5\text{N})_4\text{SiF}_6$
Cadmium tetrapyrindine fluosilicate	$\text{Cd}(\text{C}_5\text{H}_5\text{N})_4\text{SiF}_6$

When the cobalt tetrapyrindine fluosilicate is heated it loses pyridine, as represented by the reactions



The dissociation pressures of these two reactions have been measured up to a temperature of 83°.

At higher temperatures silicon tetrafluoride is also given off.

The copper, nickel, zinc and cadmium salts do not give appreciable pyridine pressures until a temperature is reached at which silicon tetrafluoride is also evolved.

NEW BRUNSWICK, NEW JERSEY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF SYDNEY]

## ALUMINO-OXALATES

BY GEORGE JOSEPH BURROWS AND KENNETH HUGH LAUDER

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The preparation of salts of alumino-oxalic acid has been described in detail by Rosenheim<sup>1</sup> who obtained derivatives of various types such as  $3\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{C}_2\text{O}_3 \cdot 9.5\text{H}_2\text{O}$ <sup>2</sup>;  $2\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 5\text{C}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$ ,  $2\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{C}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{C}_2\text{O}_3 \cdot 10.5\text{H}_2\text{O}$ . The present work was undertaken primarily with the intention of studying the mode of dissociation of the various types, other than the first, which is the normal sodium alumino-oxalate already discussed by Burrows and Walker.<sup>2</sup>

Unfortunately we have not succeeded in isolating any of these other types according to the method described by Rosenheim, using freshly

<sup>1</sup> Rosenheim, *Z. anorg. Chem.*, **11**, 175 (1896).

<sup>2</sup> The water content of this salt has already been discussed by one of us (Burrows and Walker, *J. Chem. Soc.*, **123**, 2738 (1923)).

precipitated aluminum hydroxide as the starting material. We found that in every case when aluminum hydroxide was digested with sodium binoxalate, no matter what the relative molecular proportions, the only crystalline complex salt that could be obtained was  $\text{Na}_3[\text{Al}(\text{C}_2\text{O}_4)_3]\cdot 5\text{H}_2\text{O}$ . We consider this to be the type most stable in aqueous solution.

In view of the ease with which crystalline aluminosalicylates were obtained by Burrows and Wark<sup>3</sup> by digesting aluminum ethoxide with salicylic acid in anhydrous alcohol and then adding sodium ethoxide, it was decided to attempt the preparation of the aluminooxalates in a similar manner using various molecular proportions of the different reagents.

In this manner we succeeded in isolating the acids  $\text{H}_3[\text{Al}(\text{C}_2\text{O}_4)_3]$  and  $\text{H}[\text{Al}(\text{C}_2\text{O}_4)_2]$ , together with salts of these acids and also of  $\text{H}_2[\text{Al}(\text{C}_2\text{O}_4)_2\cdot\text{OHOH}_2]$ . In the first of these types, the coordination valency of aluminum is six, the salts being isomorphous with the corresponding ferri- and chromioxalates. In the second type the metal resembles boron, its congener in the periodic table, having a coordination valency of four. The third type resembles the aluminosalicylates described by Burrows and Wark.<sup>3</sup> Wahl<sup>4</sup> succeeded in resolving the  $[\text{Al}(\text{C}_2\text{O}_4)_3]^{3-}$  ion, obtaining first the strychnine and eventually the ammonium salt of the *d*-acid. In the present investigation both *d*- and *l*-aluminum-trioxalates were isolated. Anhydrous aluminum-trioxalic acid in alcohol was treated in the cold with a solution of strychnine in chloroform and partially evaporated *in vacuo*; the strychnine salt of the *l*-form of the acid was obtained and converted into the *l*-potassium salt. When, however, the strychnine salt of the acid, obtained in the same way, was crystallized from water, the salt of the *d*-acid was obtained. Both strychnine salts were found to racemize, fairly rapidly in solution, and to a certain extent also in the solid state. The potassium salts racemized quickly.

### Experimental

**Aluminum-trioxalic Acid,  $\text{H}_3\text{Al}[(\text{C}_2\text{O}_4)_3]\cdot 9\text{EtOH}$ .**—Thin aluminum foil was converted to the ethoxide by refluxing with a trace of mercuric chloride in anhydrous ethyl alcohol. Anhydrous oxalic acid (3 moles) dissolved in alcohol was then added and the mixture warmed. The clear yellow solution which resulted was evaporated at the ordinary temperature *in vacuo* over sulfuric acid, eventually yielding a cream-colored crystalline product, readily soluble in both water and alcohol. From the analysis the acid would appear to have the composition given above.

*Anal.* Calcd. for  $\text{H}_3[\text{Al}(\text{C}_2\text{O}_4)_3]\cdot 9\text{EtOH}$ : Al, 3.9;  $\text{C}_2\text{O}_4$ , 37.4. Found: Al, 3.8;  $\text{C}_2\text{O}_4$ , 38.2.

On prolonged standing in a vacuum desiccator over sulfuric acid the compound apparently decomposes with liberation of oxalic acid.

**Aluminum-dioxalic Acid,  $\text{H}[\text{Al}(\text{C}_2\text{O}_4)_2]\cdot 4\text{EtOH}$ .**—This acid was obtained from the

<sup>3</sup> Burrows and Wark, *J. Chem. Soc.*, 133, 222 (1928).

<sup>4</sup> Wahl, *Ber.*, 60, 399 (1927).

above by standing in a vacuum desiccator over sulfuric acid for many weeks and recrystallizing from anhydrous alcohol.

*Anal.* Calcd. for  $\text{H}[\text{Al}(\text{C}_2\text{O}_4)_2] \cdot 4\text{EtOH}$ : Al, 7.0;  $\text{C}_2\text{O}_4$ , 45.4. Found: Al, 7.0;  $\text{C}_2\text{O}_4$ , 46.1.

**Trisodium Aluminum-trioxalate**,  $\text{Na}_3[\text{Al}(\text{C}_2\text{O}_4)_3] \cdot 2\text{EtOH}$ .—This salt was prepared by adding the calculated amount of sodium ethoxide (in alcoholic solution) to a solution of the tribasic aluminum-oxalic acid (in alcohol), the salt separating immediately as a copious white microcrystalline precipitate. Dried in a vacuum desiccator over sulfuric acid it was found to contain two molecules of alcohol.

*Anal.* Calcd. for  $\text{Na}_3[\text{Al}(\text{C}_2\text{O}_4)_3] \cdot 2\text{C}_2\text{H}_5\text{OH}$ : Na, 15.3; Al, 6.0;  $\text{C}_2\text{O}_4$ , 58.4. Found: Na, 15.2; Al, 6.1;  $\text{C}_2\text{O}_4$ , 57.9.

**Trianiline Aluminum-trioxalate**,  $[\text{C}_6\text{H}_5\text{NH}_2]_3[\text{Al}(\text{C}_2\text{O}_4)_3]$ .—Aniline (3 moles) was dissolved in anhydrous alcohol and added to an anhydrous alcoholic solution of aluminum trioxalic acid and the solution heated. On cooling the yellow solution so formed, a copious crop of yellow needles was obtained. In the analysis of this salt the aniline was estimated from the nitrogen content determined by the Kjeldahl method. The oxalato residue was determined by titrating an acid solution with permanganate after having previously removed the aniline by steam distillation from an alkaline solution.

*Anal.* Calcd. for  $(\text{C}_6\text{H}_5\text{NH}_2)_3\text{Al}(\text{C}_2\text{O}_4)_3$ :  $\text{C}_6\text{H}_5\text{NH}_2$ , 48.7; Al, 4.7;  $\text{C}_2\text{O}_4$ , 46.1. Found:  $\text{C}_6\text{H}_5\text{NH}_2$ , 48.5; Al, 4.7;  $\text{C}_2\text{O}_4$ , 45.7.

**Disodium Aluminum-diaquohydroxodioxalate**,  $\text{Na}_2[\text{Al}(\text{C}_2\text{O}_4)_2\text{OHOH}_2] \cdot \text{H}_2\text{O}$ .—Aluminum (1 atom) was converted to the ethoxide and treated with oxalic acid (2 moles) in anhydrous alcohol. On the addition of sodium ethoxide (2 moles), a cream-colored amorphous precipitate separated. This was extremely soluble in water. A small quantity of water was added and after refluxing for some time the salt was obtained in a microcrystalline condition. On drying at  $100^\circ$ , part of the water was driven off. The salt contained no alcohol.

*Anal.* Calcd. for  $\text{Na}_2[\text{Al}(\text{C}_2\text{O}_4)_2\text{OHOH}_2] \cdot \text{H}_2\text{O}$ : Na, 15.3; Al, 8.9;  $\text{C}_2\text{O}_4$ , 58.1. Found: Na, 15.3; Al, 8.7;  $\text{C}_2\text{O}_4$ , 58.1.

**Barium Aluminum-diaquohydroxodioxalate**,  $\text{Ba}[\text{Al}(\text{C}_2\text{O}_4)_2\text{OHOH}_2] \cdot \text{H}_2\text{O}$ .—A saturated solution of barium chloride containing the calculated amount of the salt was added to an aqueous solution of disodium aluminum-diaquohydroxodioxalate, when a precipitate separated. The latter was partly soluble in hot water, leaving a residue of barium oxalate. On cooling the hot solution the salt was obtained in a crystalline condition.

*Anal.* Calcd. for  $\text{Ba}[\text{Al}(\text{C}_2\text{O}_4)_2\text{OHOH}_2] \cdot \text{H}_2\text{O}$ : Ba, 34.8; Al, 6.8;  $\text{C}_2\text{O}_4$ , 44.6. Found: Ba, 34.5; Al, 6.6;  $\text{C}_2\text{O}_4$ , 45.0; loss at  $100^\circ$ , 10.8.

**Sodium Aluminum-dioxalate**,  $\text{Na}[\text{Al}(\text{C}_2\text{O}_4)_2] \cdot \text{EtOH}$ .—This salt was precipitated when sodium ethoxide (1 mole) was added to an alcoholic solution of aluminum-dioxalic acid prepared from aluminum ethoxide (1 mole) and oxalic acid (2 moles). The salt could not be recrystallized. On treating its aqueous solution with barium chloride, barium aluminum-diaquohydroxodioxalate  $\text{Ba}[\text{Al}(\text{C}_2\text{O}_4)_2\text{OHOH}_2] \cdot \text{H}_2\text{O}$  separated. This would indicate that the ion  $[\text{Al}(\text{C}_2\text{O}_4)_2]^-$  is unstable in aqueous solution.

*Anal.* Calcd. for  $\text{Na}[\text{Al}(\text{C}_2\text{O}_4)_2] \cdot \text{EtOH}$ : Na, 8.5; Al, 9.9;  $\text{C}_2\text{O}_4$ , 64.7; EtOH, 16.9. Found: Na, 8.5; Al, 9.9;  $\text{C}_2\text{O}_4$ , 64.5; loss at  $100^\circ$ , 15.1.

**Strychnine dl-Aluminum-trioxalate**,  $(\text{C}_{21}\text{H}_{22}\text{O}_2\text{N}_2)_2\text{H}_3[\text{Al}(\text{C}_2\text{O}_4)_3]$ .—Strychnine (3 moles) dissolved in the minimum quantity of chloroform was added to a cold alcoholic solution of tribasic aluminum-trioxalic acid (1 mole). A white precipitate separated at once but redissolved on shaking. The solution was evaporated in a vacuum desiccator over sulfuric acid, the strychnine salt crystallizing in small needles. When dry the salt was found to be insoluble in chloroform or alcohol, but readily soluble in water.

*Anal.* Calcd. for  $C_{69}H_{69}O_{18}N_8Al$ : N, 6.5; Al, 2.1;  $C_2O_4$ , 20.4. Found: N, 6.5; Al, 2.1;  $C_2O_4$ , 19.7.

In estimating the amount of oxalate ion the strychnine was precipitated by sodium hydroxide and the acidified filtrate oxidized with permanganate in the usual way.

**Strychnine *l*-Aluminum-trioxalate.**—This salt was obtained by the fractional crystallization of the racemate from a solution in alcohol containing chloroform. Owing to the fact that the dried salt was insoluble, the different fractions were kept moist with chloroform, in which solvent the salt was quite soluble. Several fractions were obtained and all were levorotatory, the first fraction giving the largest rotation. The salt underwent partial racemization in chloroform solution. Thus a solution containing 0.2 g. in 30 cc. of chloroform gave (in a decimeter tube)  $\alpha$   $-0.84^\circ$  immediately after dissolving,  $-0.60^\circ$  after half an hour,  $-0.51^\circ$  after four hours and  $-0.39^\circ$  after three days. The first reading corresponds to a value of  $[\alpha]_D -126^\circ$ . From another fraction a solution of 0.109 g. in 40 cc. of chloroform gave a rotation of  $-1.32^\circ$ , falling to  $-1.15^\circ$  in four hours. The value of  $[\alpha]_D$  corresponding to the initial reading is  $-484^\circ$ .

**Tripotassium *l*-Aluminum-trioxalate.**—This was obtained by adding a saturated aqueous solution of potassium iodide to a solution of strychnine *l*-aluminum-trioxalate in chloroform. Strychnine iodide was precipitated and chloroform removed from the filtrate under diminished pressure in the cold. The rotation of a solution (which subsequent analysis showed to contain 0.1071 gram in 20 cc.), half an hour after commencing to precipitate the strychnine, was  $-0.10^\circ$  in a decimeter tube, whence  $[\alpha]_D -19^\circ$  and  $[M]_D -11.000$ . This fell to zero after several hours. On recovering the salt from the solution it was found to be quite free from strychnine.

**Strychnine *d*-Aluminum-trioxalate,**  $[C_{21}H_{22}O_2N_2]_3H_3[Al(C_2O_4)_3]$ .—This salt was obtained in an attempt to prepare the di-strychnine salt of aluminum-trioxalic acid (in alcohol-chloroform solution as above). The first fraction which separated was the di-strychnine salt, but later fractions, on analysis, proved to be the normal compound. The product obtained by recrystallizing one crop from water was found to be dextrorotatory. Thus 0.2 g. in 40 cc. of water gave, in a decimeter tube,  $[\alpha]_D +0.43^\circ$ , immediately after dissolving, 0.00 after two hours, and  $-0.12^\circ$  after three hours, the values then remaining constant. The specific rotations corresponding to the first and last readings are  $[\alpha]_D +86^\circ$  changing to  $-24^\circ$ . The mother liquor from this crop was levorotatory.

**Tripotassium *d*-Aluminum-trioxalate.**—0.1 gram of the strychnine *d*-aluminum-trioxalate was treated in aqueous solution with excess of potassium iodide, the strychnine iodide removed and the filtrate diluted to 30 cc. The solution in a two decimeter tube gave  $\alpha_D +0.23^\circ$  immediately after dilution,  $+0.11^\circ$  after one hour,  $+0.10^\circ$  after two hours, falling to  $0.05^\circ$  after twenty-four hours. The value corresponding to the initial reading is  $[\alpha]_D +34^\circ$ .

### Summary

A description has been given of the preparation and some of the properties of aluminum-trioxalic acid, and of its trisodium, trianiline, *dl*-, *d*- and *l*-strychnine, and *d*- and *l*-tripotassium salts. Procedure is given for separating the *dl* mixture, and the ease of racemization of the isomers has been investigated.

Aluminum-dioxalic acid and its sodium salt have been prepared, as well as disodium and barium aluminum-diaquodihydroxodioxalates.