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PREPARATION AND THERMAL STABILITY OF AMMONIUM ALKALINE EARTH TRIOXALATOCOBALTATE(III) HYDRATES: $NH_4^+M^{2+}[Co(C_2O_4)_3]\cdot xH_2O$

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Trioxalatocobaltates of bivalent metals $NH_4M^{2+}[Co(C_2O_4)_3]\cdot xH_2O$, with M^{2+} = Ba, Sr and Ca, have been prepared and characterized and their thermal behaviour investigated. The compounds decompose in a complex manner to yield bivalent metal carbonate or oxide and cobalt oxide as final products. The formation of the final products is influenced by the surrounding atmosphere during decomposition. Bivalent metal cobaltite $M^{2+}CoO_{3-x}$ is not identified among the final products of decomposition. This study demonstrates the importance of the decomposition mode of the precursor in producing the desired end-product.

Ammonium trioxalatometallates [1] $(NH_4)_3[M^{3+}(C_2O_4)_3]\cdot 3H_2O$, where M^{3+} = Fe, Al and Cr, are reported to decompose to yield M_2O_3 as the final product. We have been interested in identifying precursors which could be employed in low-temperature chemical methods for the preparation of perovskite-type oxides. Alkaline earth cobaltites $M^{2+}CoO_{3-x}$ are generally prepared by the ceramic method, by the solid-state reaction between the individual carbonates or oxides above 1273 K. The compounds $NH_4^+M^{2+}[Co(C_2O_4)_3]\cdot xH_2O$ have been prepared and studied as possible psecursors for $M^{2+}CoO_{3-x}$. The study reveals the importance of the decomposition mode of the precursors in obtaining the desired end-product.

Experimental

Materials

All the reagents used were of either BDH "Analar" or E. Merck "pro analysi" grade. A solution of the alkaline earth salt (nitrate, chloride or acetate) (1 M) was

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added slowly with stirring to an aqueous solution of ammonium trioxalatocobaltate (2 M). The mixture was stirred well, cooled in ice, and the precipitate was filtered off, washed with dilute (1 : 1) alcohol, then with acetone, and air-dried. The procedure was slightly modified for the calcium salt. After mixing of the reagents, acetone was added to precipitate the calcium salt. The precipitate was filtered off, washed with a 1 : 1 acetone-water mixture and finally with acetone, and air-dried. The compounds $NH_4^+M^{2+}[Co)C_2O_4)_3] \cdot xH_2O$ with M^{2-} = Ba, Sr and Ca have been prepared.

Methods

The physical techniques employed, such as TG, DTA, DTG, IR spectroscopy and X-ray powder diffraction, have been described in an earlier publication [2].

Barium was estimated gravimetrically as sulphate. Calcium and strontium were estimated complexometrically by titration with EDTA at pH 12 after masking cobalt with cyanide and employing calcein and methyl thymol blue, respectively, as indicators. Cobalt was estimated volumetrically by titration with EDTA at pH 5.6, employing methyl thymol blue as indicator. Ammonia was estimated by the standard Kjeldahl method. Oxalate was determined by the permanganate method. Water content was determined gravimetrically by decomposing a known weight of the material and absorbing the evolved water in anhydrous magnesium perchlorate.

Gaseous products were identified with an MS 10 mass spectrometer; the procedure for their quantitative analysis has been described in a previous communication [2].

Results

The trioxalatocobaltates have the general formula $NH_4M^{2+}[Co(C_2O_4)_3] \cdot xH_2O$, where M^{2+} = Ba, $x = 3$ or M^{2+} = Sr, Ca, $x = 4$. The complete analytical data for these complexes are given in Table 1. The compounds are green in colour and are diamagnetic. The calcium salt is readily soluble in water, while the other two are fairly soluble. All the complexes are crystalline; their X-ray powder diffraction data are presented in Table 2. The patterns cannot be indexed on the basis of high-symmetry classes such as cubic, tetragonal or hexagonal. The IR spectra of these compounds are similar and all the bands could be assigned by comparison with those of ammonium trioxalatocobalt(III) trihydrate and other oxalato complexes [3].

Table 1 Analytical data on $NH_4^+M^{2+}Co(C_2O_4)_3 \cdot xH_2O$

Compound	% NH_3	% M^{2+}	% Co	% C_2O_4
$NH_4Ba[Co(C_2O_4)_3] \cdot 3H_2O$ Obs.	2.94	25.66	10.89	48.15
Calcd.	3.19	25.80	11.07	49.59
$NH_4Sr[Co(C_2O_4)_3] \cdot 4H_2O$ Obs.	3.10	17.24	11.91	50.15
Calcd.	3.39	17.50	11.77	52.74
$NH_4Ca[Co(C_2O_4)_3] \cdot 4H_2O$ Obs.	3.55	9.07	13.16	56.74
Calcd.	3.75	8.84	13.00	58.27

Table 2 X-ray powder diffraction data on the compounds $NH_4^+M^{2+}[Co(C_2O_4)_3] \cdot xH_2O$

ABCO		ASCO		ACCO	
d, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0
8.580	100	8.261	100	8.036	100
6.856	90	6.231	50	6.103	65
5.034	65	5.569	8	4.666	25
4.206	30	5.453	7	4.036	20
3.735	85	5.272	10	3.689	30
3.644	25	5.211	10	2.760	10
		4.886	15		
		4.791	10		
		4.642	25		
		4.287	10		
		4.199	20		
		4.148	15		
		4.054	7		
		3.750	40		
		3.385	7		
		3.118	9		
		2.966	7		
		2.769	7		
		2.712	10		
		2.604	10		

The thermal decomposition of these compounds was carried out in atmospheres of flowing air, carbon dioxide and a vacuum. The compounds decompose in a stepwise manner to yield cobalt oxide and either the carbonate or oxide of the bivalent alkaline earth metal. Alkaline earth cobaltate has not been identified among the final products of decomposition.

Ammonium barium trioxalatocobaltate(III) trihydrate (ABCO)

Figures 1 and 2 present the thermal curves of ABCO in atmospheres of air, carbon dioxide and a vacuum. The temperature ranges and weight losses for the different steps of the decomposition are given in Table 3.

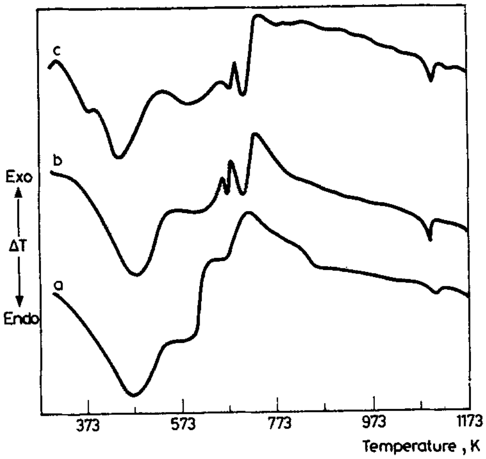

Fig. 1 DTA of ABCO in (a) air, (b) carbon dioxide, and (c) a vacuum

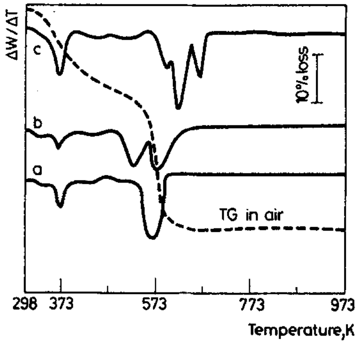

Fig. 2. TG and DTG curves of ABCO in (a) air, and DTG curves of ABCO in (b) carbon dioxide and (c) vacuum

Dehydration of the hydrate

The dehydration of ABCO takes place in the temperature range 313–498 K, with a weight loss of 18.0 to 18.5 per cent. These values are considerably higher than the calculated value of 10.15 per cent for the removal of only $3H_2O$ mole^{-1}. The

Table 3 Temperature ranges and weight losses for ABCO in different atmospheres

Gas atmosphere		Air		Carbon dioxide		A vacuum	
Decomposition step	Calcd. % wt. loss	Temp. range, K	% wt. loss	Temp. range, K	% wt. loss	Temp. range, K	% wt. loss
Partial dehydration accompanied by partial oxalate decomposition	15.02	313–423	14.0	313–448	13.5	313–473	18.5
Complete dehydration	3.38	423–498	4.0	448–533	4.0		
Decomposition of the oxalate	29.43	498–773	28.5	533–773	29.0	473–773	30.0
Total weight loss	47.83		46.5		46.5		48.5

isothermal heating of ABCO at 383 K leaves behind a pink residue of composition $NH_4Ba[Co(C_2O_4)_{2.5}]\cdot H_2O$ and the analysis of the evolved gases indicates the presence of carbon dioxide along with water vapour. The observed weight loss at this stage is 15.94 per cent. If ABCO is decomposed isothermally at 423 K, it suffers a total weight loss of 18.16 per cent and the evolved gases are again carbon dioxide and water only. The residue corresponds to $NH_4BaCo(C_2O_4)_{2.5}$. Thus, dehydration takes place in two steps. The first step is accompanied by a partial decomposition of the oxalate and a reduction of Co(III) to Co(II). This occurs in the temperature range 313–423 K, with a weight loss of 14.5 to 16.0 per cent, and involves the loss of $(2H_2O+CO_2)$ per mole ABCO. The remaining water is lost slowly in the temperature range 423–498 K, with a loss of 3.8 to 4.0 per cent in weight. The dehydrated compound is amorphous to X-rays, and its IR spectrum (Fig. 3) shows the principal oxalate absorption band at around 1650 cm^{-1}. The aqueous extract of the residue shows the presence of ammonium oxalate, which can be recovered almost quantitatively.

Decomposition of the oxalate

The decomposition of the oxalate is a multistep process. The first step of oxalate decomposition overlaps the dehydration step. The major step of oxalate decomposition is observed in the temperature range 498–823 K and is accompanied by a weight loss of 28.5 per cent. The DTG in air shows this to be a single peak. However, the DTA and DTG in carbon dioxide and a vacuum exhibit more peaks. The isothermal heating of ABCO at 493 K results in a weight loss of 30.06 per cent, and the analysis of the residue corresponds to the composition $BaC_2O_4\cdot CoC_2O_4$.

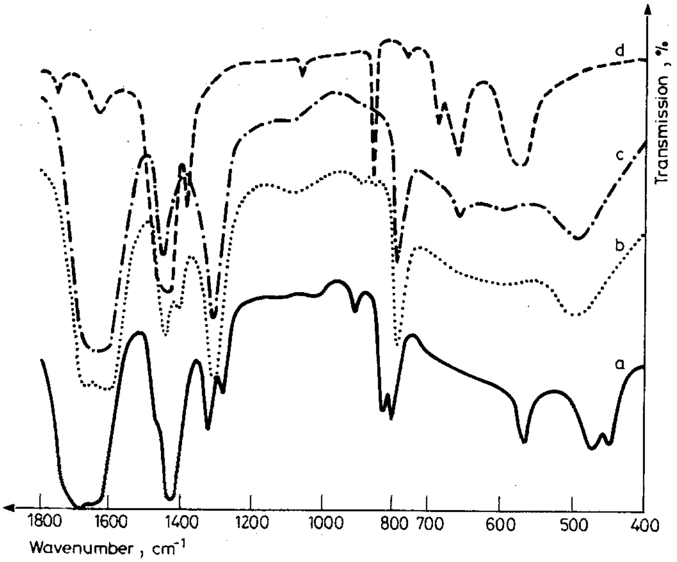

Fig. 3. IR spectra of (a) ABCO (b) ABCO (423 K) (c) ABCO (493 K) and (d) ABCO (593 K)

The gaseous products evolved show the presence of ammonia, water, carbon monoxide and carbon dioxide. The infrared spectrum of the residue displays the absorption bands of a simple oxalate. Isothermal heating of ABCO at 593 K results in a weight loss of 45.77 per cent. The gaseous products are again carbon monoxide, carbon dioxide and traces of ammonia and water vapour. The ratio of CO : CO_2 at this temperature is found to be 1 : 1.46. The oxalate decomposition is shifted to a higher temperature in carbon dioxide atmosphere and a vacuum. It is exothermic in air and endothermic both in carbon dioxide and in a vacuum. The infrared spectrum of the residue at 593 K clearly shows the bands due to a carbonate. The X-ray powder diffraction data of this residue indicate the presence of $BaCO_3$ and Co_3O_4. No further weight loss is observed beyond 773 K. However, the DTA curves show a small endotherm beyond 1073 K. This is attributed to the reversible phase transformation of barium carbonate. The X-ray powder diffraction data on the DTA residue at 1173 K also indicate the presence of only barium carbonate ($BaCO_3$) and cobalt oxide (Co_3O_4).

Discussion

Based on the above results, the following scheme has been proposed for the decomposition of ABCO in air:

$$NH_4Ba[Co^{3+}(C_2O_4)_3]\cdot 3H_2O \xrightarrow{313\text{–}378\ K} NH_4BaCo^{2+}(C_2O_4)_{2.5}\cdot H_2O + \\ + 2\,H_2O + CO_2 \ldots \qquad (1)$$

$$NH_4BaCo^{2+}(C_2O_4)_{2.5}\cdot H_2O \xrightarrow{423\text{–}498\ K} NH_4BaCo^{2+}(C_2O_4)_{2.5} + H_2O \qquad (2)$$

$$NH_4BaCo^{2+}(C_2O_4)_{2.5} \xrightarrow{498\text{–}773\ K} BaCO_3 + 1/3\,Co_3O_4 + \\ + NH_3 + 0.5\,H_2O + 2.83\,CO + 1.17\,CO_2 \ldots \qquad (3)$$

Equations (1) and (2) correspond to dehydration accompanied by partial decomposition of the oxalate. On the completion of the dehydration step, the residue is probably an intimate mixture of ammonium oxalate, barium oxalate and cobaltous oxalate. These oxalates decompose in the temperature range 498–773 K. The decompositions overlap one another and result in the formation of barium carbonate and cobalt oxide (Co_3O_4). Isothermal heating studies indicate that ammonium oxalate decomposes first endothermically, followed by the decomposition of barium and cobalt oxalates to produce barium carbonate and cobalt oxide (Co_3O_4), respectively. There is no indication of the formation of barium cobaltite, $BaCoO_{3-x}$. In a vacuum and in carbon dioxide, along with barium carbonate, CoO and metallic cobalt are found to be the final products of decomposition.

Ammonium strontium trioxalatocobaltete(III) tetrahydrate (ASCO) and ammonium calcium trioxalatocobaltate(III) tetrahydrate (ACCO)

The decomposition patterns of ASCO and ACCO exhibit a general similarity to that of the barium analogue. However, they show some extra features. ASCO undergoes dehydration in two steps evolving ($2H_2O+CO_2$) and $2H_2O$ mole^{-1}, respectively, in the temperature range 313–493 K. Here again, the first dehydration step is accompanied by partial decomposition of the oxalate. Further decomposition of the oxalate occurs in two steps in the temperature regions 493–573 K and 573–773 K, respectively. In the first step, ammonium carbonate and the oxalates of strontium and cobalt are produced. The presence of ammonium carbonate is shown in the aqueous extract of the residue obtained by heating ASCO at 473 K for 2 hours. The final residue of the decomposition is a mixture of strontium carbonate and cobalt oxide (Co_3O_4).

The decomposition pattern of ACCO, though similar to that of the strontium complex, shows additional features. Dehydration takes place in one step in the temperature range 313–523 K. This is accompanied by partial decomposition of the oxalate. In the DTA of ACCO, the endothermic dehydration is immediately followed by a sharp exotherm. The exotherm may be attributed to the breaking up of an active (energy-rich) complex $NH_4CaCo(C_2O_4)_{2.5}^*$ to the individual oxalates [4]. The oxalates further decompose to a mixture of calcium carbonate and cobalt oxide (Co_3O_4) in the temperature region 523–773 K. There is a further weight loss in the temperature region 973–1173 K, which is attributed to the decomposition of calcium carbonate to calcium oxide and carbon dioxide. From the X-ray powder diffraction pattern, the final residue has been identified as a mixture of calcium oxide and cobalt oxide (Co_3O_4).

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Zusammenfassung — Trioxalatokobaltate zweiwertiger Metalle der allgemeinen Formel $NH_4M^{2+}[Co(C_2O_4)_3]\cdot xH_2O$ (M^{2+} = Ba, Sr, Ca) wurden dargestellt, charakterisiert und hinsichtlich ihres thermischen Verhaltens untersucht. Die Verbindungen zersetzen sich in komplexer Weise unter Bildung von Carbonaten und Oxiden der zweiwertigen Metalle und Kobaltoxid als Endprodukte. Die Bildung der Endprodukte wird durch die die Proben während der Zersetzung umgebende Atmosphäre beeinflußt. Kobaltite der zweiwertigen Metalle, $M^{2+}CoO_{3-x}$, treten nicht als Endprodukte auf. Die Untersuchung zeigt, wie wichtig die Art der Zersetzung des Präkursors für die Darstellung erwünschter Endprodukte ist.

Резюме — Исследовано термическое поведение синтезированных триоксалатокобальтатов двухвалентных металлов общей формулы $NH_4M^{2+}[Co(C_2O_4)_3]\cdot xH_2O$, где M^{2+} — барий, стронций и кальций. Соединения разлагаются сложным путем, давая карбонат двухвалентного металла или же в качестве конечного продукта окись этого металла и окись кобальта. Образование конечных продуктов разложения зависит от окружающей атмосферы в процессе разложения. Кобальтит двухвалентного металла $M^{2+}CoO_{3-x}$ не установлен среди конечных продуктов разложения. Проведенное исследование свидетельствует о важности типа разложения предшествующего соединения при получении желаемого соединения и образующегося.