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STUDIES ON THE THERMAL DECOMPOSITIONS OF HETEROPOLYNUCLEAR GLYOXYLATES OF Cr(III) AND Cu(II)

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Abstract

Complexes of Cr(III):Cu(II) with the glyoxylate dianion as ligand were synthesized in the range of cation atomic ratios (0.01–8):1.0.

The results of non-isothermal analysis of the synthesized compounds correlated with the results of IR and UV-VIS spectroscopy, and gas chromatography of the volatile products of the decomposition allowed the formulation of a mechanism for the decomposition of the complex with Cr(III):Cu(II)=2:1 and the assumption that the other complexes are mixtures of this with the homopolynuclear complexes of Cr(III) and Cu(II), depending on the ratio of the cations Cr(III):Cu(II).

The thermal conversion of the complexes takes place at relatively low temperatures, with partial transformation of the ligand into oxalate and of the oxide mixture into $CuCrO_4$.

Keywords: decomposition mechanism, glyoxylates, heteropolynuclear complexes, thermal analysis

Introduction

Complex heteropolynuclear combinations in which the cations are situated in the same coordination sphere and which decompose at low-temperature to form mixed oxides comprise a very interesting field for investigation.

The ligands are usually anions of carboxylic acids [1–3] (formate, acetate, oxalate, glycolate, etc.). Such complex combinations generally undergo thermal conversion to produce amorphous oxides with very fine granulation and high-reactivity. Accurate thermal treatment of such compounds may provide compounds with controlled properties (catalytic activity, specific surface, etc.) [4].

During recent years, a new method of obtaining complex homo- and heteropolynuclear complex combinations containing the glyoxylate dianion $[HC(OH)O–COO]^{2-}$, $C_2H_2O_4^{2-}$ (GA), as ligand, has been elaborated. It consists in the hot oxidation (at about 100°C) of 1,2-ethanediol, ethyleneglycol (EG), to the glyoxylate dianion in aqueous solution by nitrates of certain metals. The complex glyoxylates are isolated in the solid state [5–7].

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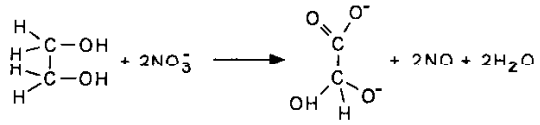
The proposed method has the advantages that the complexes are obtained in a short time, in a yield of practically 100%. The redox reaction may be written as follows:



(EG) (GA)

This paper reports a study of the thermal behaviour of the heteropolynuclear glyoxalates of Cr(III):Cu(II) with atomic ratios (0.01–8):1.

In order to establish the mechanism of the thermal conversion, analytical methods were used: thermal analysis in air and nitrogen, gas chromatography, IR and UV-VIS spectroscopy.

Experimental

The complexes were synthesized by a recently proposed method [5–7], from the reagents 1,2-ethanediol (Fluka), $Cr(NO_3)_3 \cdot 9H_2O$ (Merck) and $Cu(NO_3)_2 \cdot 3H_2O$ (Merck). Details concerning the synthesis are presented in previous papers [6–8]. Appropriate amounts of compounds were used in order to obtain the atomic ratios detailed in Table 1.

Table 1 Atomic ratios Cr(III):Cu(II) and colours of the synthesized products

Sample	1	2	3	4	5	6	7	8	9
Cr(III)	0.01	0.02	0.03	0.10	0.50	1.00	2.00	3.70	8.00
Cu(II)	←	———	———	———	1.00	———	———	———	→
Colour	←	db*	→	g**	———	dg***	———	———	→

*db – dark blue; **g – green; ***dg – dark green

The synthesized compounds, which are insoluble in water or the usual organic solvents, were characterized by elemental (Cr(III), Cu(II), C, H, $C_2H_2O_4^{2-}$) analysis, thermal analysis, electronic diffuse reflectance and IR spectroscopy [7].

The thermal analysis of the compounds was carried out with a 1500D Derivatograph (MOM, Budapest), in plate-type crucibles, at a heating rate of 5°C min^{-1}, in static air atmosphere and flowing nitrogen atmosphere of 100 ml min^{-1}. The mass of sample taken for each compound was 100 mg.

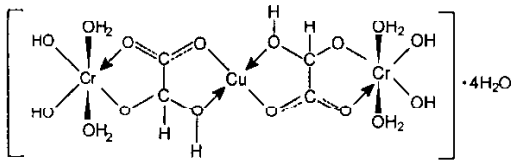
Study of the thermal behaviour of all the compounds was accompanied by the thermogravimetric analysis of certain intermediates obtained by heating at temperatures of 100°C (P_{100}), 160°C (P_{160}), 205°C (P_{205}), 227°C (P_{227}), 290°C (P_{290}), 350°C (P_{350}) and 453°C (P_{453}), and stabilized by cooling in nitrogen in an Ugine-Eyraud balance.

The IR spectra of the glyoxylates in KBr pellets and of some of the intermediates or end-products were recorded with a Specord M 80 spectrophotometer (Carl Zeiss, Jena). The Cr(VI) present in the samples subjected to conversion in air was analysed with a Specord UV-VIS spectrophotometer (Carl Zeiss, Jena).

The volatile products resulting from thermal decomposition were analysed by gas chromatography on a GCHF 18.3 instrument, with a 3 mm×3 m column filled with Porapak Q (80–100 mesh).

Results and discussion

The elemental analysis results, the diffuse reflectance electronic spectra and the IR spectra, together with the fact that the glyoxylate dianion acts as a double-bridge ligand in other homo- and heteropolynuclear complexes [7, 8], led to the postulation of possible formulae and structures for the Cr(III), Cu(II) and 2Cr(III)–Cu(II) glyoxylates, as depicted below for compound **7**: $[Cr_2Cu(GA)_2(OH)_4(OH_2)_4]\cdot 4H_2O$ (Table 1).



The Cr(III) ion is in a pseudo-octahedral environment and the Cu(II) in a square-planar one.

Figure 1 presents curves relating to the thermal conversion of 2Cr(III)–Cu(II) glyoxylate in air or nitrogen.

The crystallization water is lost within the temperature range 30–180°C, to the accompaniment of an endothermic effect, both in air and in nitrogen.

Additionally, in air there occur processes of decomposition and burning of the ligand in the range 180–320°C, and crystallization of amorphous Cr_2O_3 in the range 400–420°C, all with exothermic effects.

In nitrogen, the decomposition of the complex takes place in a wider temperature range (180–480°C), with a slight exothermic effect assigned to the crystallization of amorphous Cr_2O_3.

The solid product of the decomposition at 500°C consists of partially crystallized mixture of α-Cr_2O_3 and CuO; its mass is in agreement with the stoichiometry of the initial compound, both in air and nitrogen.

A more detailed resolution of the thermal conversion steps was achieved by thermal analysis and IR spectroscopy on samples P_{100}, P_{160}, P_{205}, P_{227}, P_{290}, P_{350} and P_{453}. The TG curves and the corresponding IR spectra, together with those of the initial compounds, are shown in Figs 2 and 3.

From the TG curves, it was possible to establish more accurately the temperature ranges associated with the decomposition steps and the corresponding mass losses.

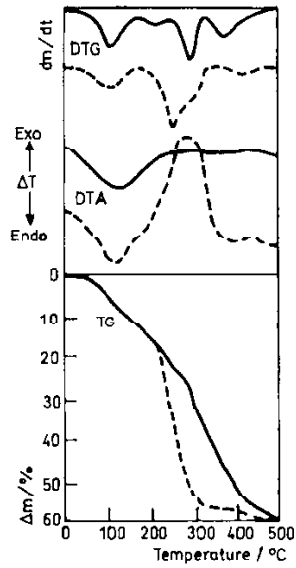


Fig. 1 Thermal curves of $[Cr_2Cu(GA)_2(OH)_4(OH_2)_4]\cdot 4H_2O$ in air (- - -) and nitrogen (—)

The IR spectra of samples P_{100}, P_{160} and P_{205} are practically identical with those of sample **7**.

However, in the spectrum of sample P_{205} there is a shoulder at 610 cm^{-1} that is characteristic of the Cu(I)–O bond, and thus a redox interaction between Cu(II) and the glyoxylate dianion may be presumed.

The spectrum of sample P_{227} reveals significant modifications, as follows: the bands at 1365 [ν(C–O*)] and 1310 cm^{-1} [δ(COH)] resemble those of the oxalate; the band at 820 cm^{-1} [δ_{as}(OCO)] and the shoulder at 610 cm^{-1} (Cu(I)–O) are missing; in general, all the bands are of lower intensity. Thus, a partial transformation of the ligand into oxalate and its decomposition may be presumed; such an assumption is supported by the TG curve (Fig. 2).

The IR spectrum of sample P_{290} exhibits a band at 930 cm^{-1}, characteristic of the Cr(VI)–O bond in $CuCrO_4$, and a significant lowering of the other bands, less than the broad band at 500 cm^{-1}, which is characteristic of the M–O bond.

The IR spectrum of sample P_{350} exhibits only bands at 1600 cm^{-1} [assigned to the vibration $\nu_{as}(COO^-)$], 930 cm^{-1} (more pronounced) and 500 cm^{-1}.

In the spectrum of sample P_{453}, only the band corresponding to the M–O bonds occurs, split into two maxima, at 610 and 570 cm^{-1}, characteristic of the Cr(III)–O bond in α-Cr_2O_3 (as a result of decomposition of the chromate and the crystallization of Cr_2O_3).

Gas chromatographic analysis of the volatile products of the thermal conversion of complex **7** revealed the evolution of carbon dioxide, starting at 230°C.

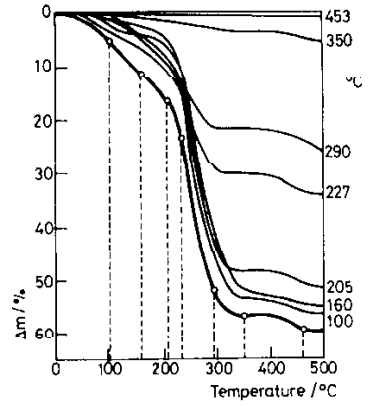


Fig. 2 Thermal curves of the initial complex combination (i) and after heating at 100°C (P_{100}), 160°C (P_{160}), 205°C (P_{205}), 227°C (P_{227}), 290°C (P_{290}) 350°C (P_{350}) and 453°C (P_{453})

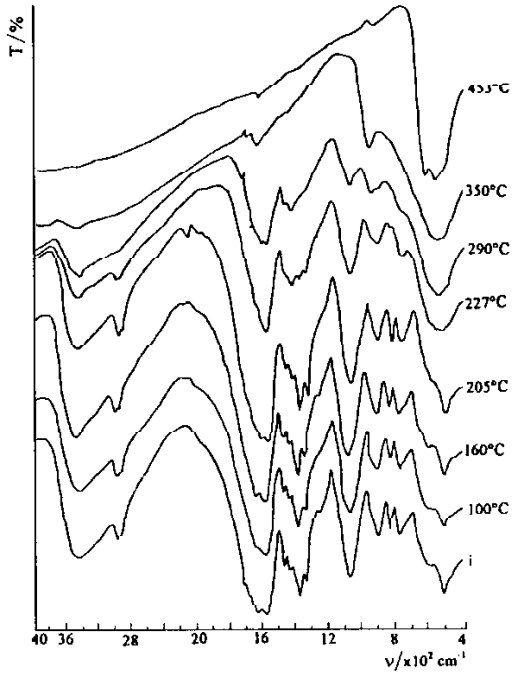


Fig. 3 IR spectra of the initial complex combination (i) and after heating at 100°C (P_{100}), 160°C (P_{160}), 205°C (P_{205}), 227°C (P_{227}), 290°C (P_{290}), 350°C (P_{350}) and 453°C (P_{453})

Sample **7** was studied comparatively, as far as the thermal evolution is concerned, with a mechanical mixture of the homopolynuclear complexes of Cr(III) and Cu(II) in a molar ratio of 2:1. The thermal curves for the mechanical mixture reveal the existence of the thermal decomposition steps characteristic of the homopolynuclear complexes of Cr(III) and Cu(II), accompanied by the corresponding thermal effects [8], unlike the thermal curves of compound **7**, where these steps could not be observed.

Consequently, the following overall mechanism is proposed for the thermal conversion of 2Cr(III)/Cu(II) glyoxylate in air:

$$[Cr_2Cu(C_2H_2O_4)_2(OH)_4(OH_2)_4]\cdot 4H_2O \xrightarrow{30-180^{\circ}C}$$

$$4H_2O_{(g)} + Cr_2Cu(C_2H_2O_4)_2(OH)_4(OH_2)_4 \xrightarrow{180-225^{\circ}C}$$

$$(4+x)H_2O_{(g)} + Cr_2(III)Cu(II)_{(1-x)}Cu(I)_x(C_2H_2O_4)_{(2-x/2)}(C_2O_4)_{x/2}(OH)_{(4-x)}$$

$$\xrightarrow{225-325^{\circ}C} (4-x)H_2O_{(g)} + 4CO_{2(g)} + yCuCrO_4 + (2-y)Cr_2O_{(3+z)} + (1-y)CuO$$

$$(2-y)Cr_2O_{(3+z)} \xrightarrow{400-420^{\circ}C} (2-y)\alpha\text{-}Cr_2O_3 + z/2O_2$$

$$yCuCrO_4 \xrightarrow{420-450^{\circ}C} y/2CuCr_2O_4 + y/2CuO$$

Table 2 DTG and DTA data on the thermal decompositions of the studied complexes

Compound	DTG, T_{max}/°C	DTA, T_{max}/°C
Homopolynuclear complex of Cu(II)	90, 175, 185	(+)195
1	90, 180, 190	(+)195
2	90, 180, 200	(+)210
3	90, 180, 200	(+)210
4	90, 180, 205	(+) 210
5	90, 180, 220, 400	(+)240, (+)410
6	105, 210, 400	( )110, (+)240, (+)410
7	105, 250, 410	(–)110, (+)280, (+)420
8	105, 250, 410	(–)110, (+)280, (+)420
9	105, 270, 410	(–)110, (+)300, (+)420
Homopolynuclear complex of Cr(III)	105, 270, 400	(–)110, (+)290, (+)410

(+) exothermal effect; (–) endothermal effect

It may be noted that complexes **1**, **2**, **3** and **4** exhibit thermal behaviour resembling that of the homopolynuclear complex of Cu(II), whereas the behaviour of complex **9** resembles that of the homopolynuclear complex of Cr(III) [8]; the other complexes with intermediate compositions, i.e. **5**, **6** and **8**, exhibit the common charac-

teristics of the heteropolynuclear complex **7** and the homopolynuclear complexes of Cr(III) and Cu(II), depending on the composition (Table 2).

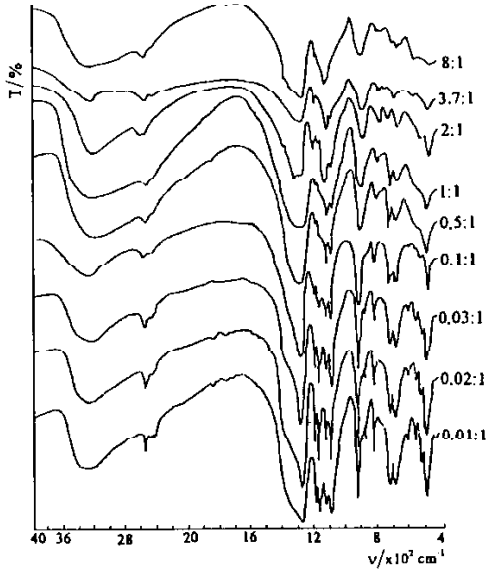


Fig. 4 IR spectra of the studied complex combinations (Table 1)

The IR spectra (Fig. 4) of the complex combinations from Table 1 confirm the thermal analysis results. Thus, there is a change in the spectrum, from that practically identical with the spectrum of the complex homopolynuclear combination of Cu(II) (sample **1**) to a spectrum resembling that of sample **7**, for sample **6**, but which retains the important bands of the former.

A similar observation holds for samples **8** and **9**, where sample **9** has a spectrum practically identical to that of the homopolynuclear combination of Cr(III), while the spectrum of sample **8** exhibits characteristics common with those of sample **7** and the homopolynuclear complex of Cr(III).

These observations lead to the assumption that samples **1**, **2**, **3**, **4**, **5**, **6**, **8** and **9** are mixtures of the heteropolynuclear complex combination 2Cr(III):Cu(II) and the homopolynuclear complex of Cu(II) or Cr(III), depending on the ratio Cr(III):Cu(II).

Conclusions

Of the complex combinations of Cr(III):Cu(II) with the glyoxylate dianion as ligand in the range of atomic ratios of the cations (0.01–8):1.0, only the complex with the ratio Cr(III):Cu(II)=2:1 behaves as a unitary compound on decomposition. The other complexes are probably mixtures of the heteropolynuclear complex Cr(III):Cu(II)=2:1 and the homopolynuclear complexes of Cr(III) or Cu(II).

Non-isothermal analysis of the heteropolynuclear complex with Cr(III):Cu(II)= 2:1, in the initial state and after various stages of thermal decomposition, associated with the results of IR and UV-VIS spectroscopy and gas chromatography of the volatile decomposition products, allowed the proposal of a thermal conversion mechanism. This included partial decomposition of the ligand through oxalate and the transformation into copper chromate of part of the solid end-product of the decomposition up to 500°C.

The complex combinations Cr(III):Cu(II) with the glyoxylate dianion decompose at relatively low temperatures and furnish oxide mixtures with enhanced reactivity.

Further, the presence of $CuCrO_4$ in the oxide mixtures favours the formation of $CuCr_2O_4$ at low temperatures [9–11].

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