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THE PREPARATION AND THERMAL DECOMPOSITION OF TWO DIAMINOGLYOXIME COMPLEXES

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ABSTRACT

Two new cobalt diaminoglyoxime complexes have been prepared under SO_2 and NO atmospheres and their thermal decomposition investigated using TG–DTG–DTA techniques simultaneously.

INTRODUCTION

Diaminoglyoxime, which was synthesized by Fischer[1] and later by Tiemann et al.[2], has an important place in coordination chemistry. To further investigate the complexes made with diaminoglyoxime, Tschugaeff and Surenjanz[3] have also synthesized the nickel complexes. The complexes produced by the reaction of diaminoglyoxime with various transition metals have also been investigated by several other scientists[4–20].

In all the above studies, different structures have been proposed. In 1962, Ungnade[21], by means of NMR and IR spectrophotometric techniques, demonstrated that diaminoglyoxime has a *trans* structure. Recently, some new complexes have been produced with diaminoglyoxime. One of them was bis(diaminoglyoximato)cobalt(II) diaminoglyoxime, synthesized by the reaction of cobalt(II) acetate with diaminoglyoxime under a N_2 atmosphere[22]. The structure of this compound has been analysed for the first time by means of a single crystal refractometer[23].

In this work are described the complexes which are isolated with cobalt(II) under SO_2 and NO atmospheres, as well as their thermal decomposition.

EXPERIMENTAL

Preparation of $[(C_4H_{12}N_8O_7S)Co]\cdot 2H_2O$

Diaminoglyoxime was prepared according to Fischer's method[1]. Hydratobis-(diaminoglyoximato)(sulphurdioxide) cobalt(II): 1.18 g (10^{-2} mol) diaminoglyoxime

TABLE 1

ANALYSIS OF $[(C_4H_{12}N_8O_7S)Co] \cdot 2H_2O$

	C (%)	H (%)	N (%)	S (%)	Co (%)
Theoretical composition	11.68	3.89	27.25	7.78	14.35
Analytical results	11.94	3.53	26.73	7.76	14.41

TABLE 2

ANALYSIS OF $[(C_4H_{12}N_9O_6)Co] \cdot 2H_2O$

	C (%)	H (%)	N (%)	Co (%)
Theoretical composition	12.73	4.24	33.42	15.65
Analytical results	13.14	4.03	33.17	16.05

was dissolved in 70 ml of hot water. Afterwards, SO_2 was passed through it and a solution of 1.19 g ($5 \cdot 10^{-3}$ mol) $CoCl_2 \cdot 6H_2O$ in 30 ml of water was added. SO_2 was then passed through the mixture continuously for 24 h.

The precipitated crystals (in the shape of orange leaves) were washed with alcohol/ether after filtration and then vacuum dried. After 10 h, a sample of this freshly prepared compound at 110°C shows a weight loss which corresponds to two molecules of water (see Table 1).

Preparation of $[(C_4H_{12}N_9O_6)Co] \cdot 2H_2O$

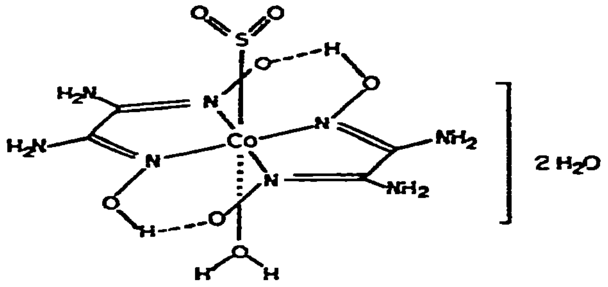
NO was passed through a solution of 1.19 g ($5 \cdot 10^{-3}$ mol) $CoCl_2 \cdot 6H_2O$ in 30 ml of hot water and 1.18 g (10^{-2}) diaminoglyoxime dissolved in 70 ml hot water. The pH of this solution was adjusted to pH 8 with 2 ml of a saturated solution of NH_4OH. After a few minutes, black crystals were separated from the solution. The precipitated black crystals were washed with alcohol/ether after filtration and vacuum dried. After 10 h, a sample of this compound at 110°C shows a weight loss which corresponds to two molecules of water (see Table 2).

EQUIPMENT

Thermal analyses (simultaneous TG–DTG–DTA) were carried out using a Mettler Thermoanalyzer TA1. The experiments were made under the same experimental conditions in dry air, nitrogen and argon (730 torr), at a gas flow rate of 5 l/h. The DTA sample holder (DTA11, Ni/CrNi thermocouple) was used with Al crucibles (0.1 cm^3). In order to work in a definite inert atmosphere such as N_2 or argon, a change of the atmosphere with the prevacuum system must be made. Therefore, the determined weight loss of crystal water (a certain weight loss occurs during the atmosphere exchange) is smaller than expected.

RESULTS AND DISCUSSION

SO_2–Co complex



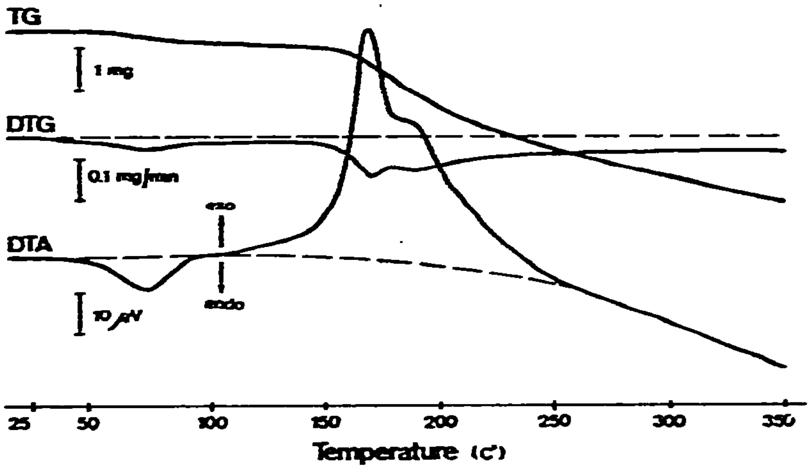


Fig. 1. TG, DTG and DTA curves of the SO_2-Co complex measured simultaneously in air, heating rate 2 K min^{-1}, sample weight: 9.15 mg.

TABLE 3

TG, DTA AND TEMPERATURE DETAILS FOR THE DECOMPOSITION OF THE SO_2–Co COMPLEX IN DIFFERENT ATMOSPHERES UP TO 350 °C

Atmosphere	*Weight loss, step 1*			*Weight loss, step 2*		
	Temp. range (°C)	*DTA*	*%*	*Temp. range (°C)*	*DTA*	*%*
Synth. air	25–100	Endo	3.8	100–250	Exo	27.6
N_2	30–100	Endo	3.5	100–250	Exo	26.4
Argon	40–100	Endo	1.8	100–250	Exo	26.9

The investigation of $[(C_4H_{12}N_8O_7S)Co] \cdot 2H_2O$ in air (Fig. 1) shows two weight steps in the temperature range 25–350°C. The separation of these steps is possible with the help of the DTG and DTA curves. Weight step 1 of 3.8% (Table 3) in the temperature range 25–100°C represents the crystal water release. The calculated value of the weight loss corresponding to two crystal water molecules is 8.76%; the SO_2–Co complex therefore seems to contain only one crystal water molecule as a result of weathering of the complex at room temperature. The decomposition reaction between 100 and 250°C is strongly exothermic. Both the DTA and the DTG curves reveal that there must be two strongly overlapping reactions; a separation is not possible, even at a slow heating rate of 2 K min^{-1}. Weight step 2 of 27.6% represents the release of SO_2, coordinately bonded water, and NH_3. The end of weight step 3

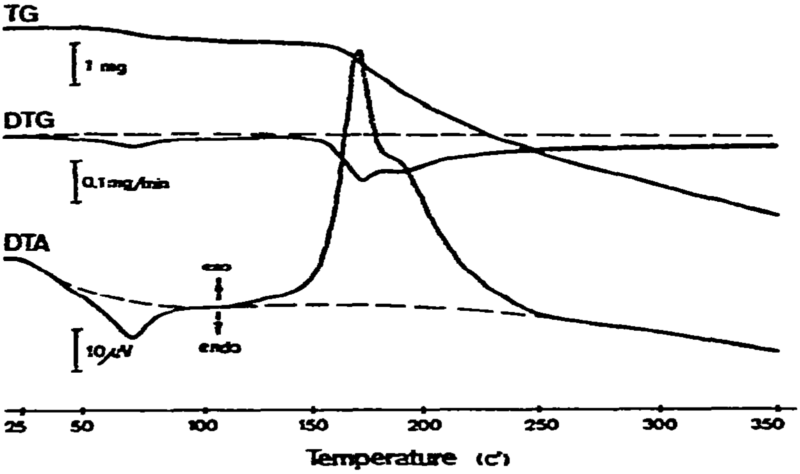


Fig. 2. TG, DTG and DTA curves of the SO_2–Co complex measured simultaneously in nitrogen, heating rate 2 K min^{-1}, sample weight: 10.04 mg.

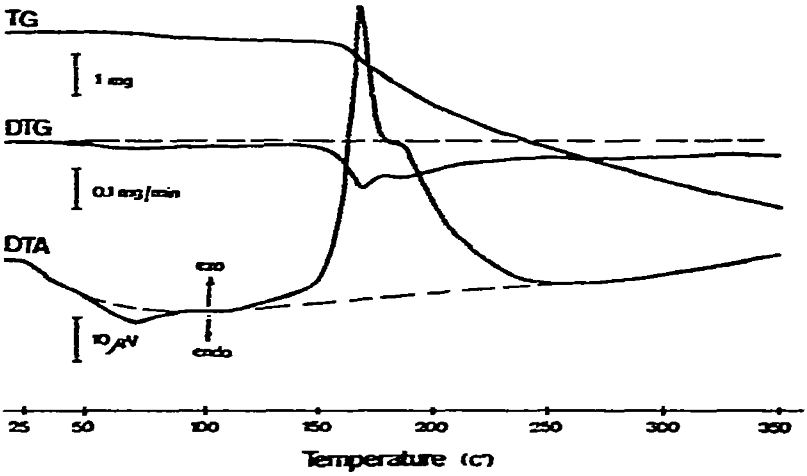
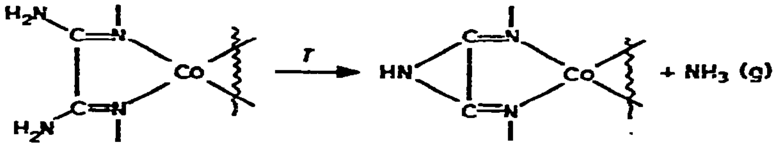


Fig. 3. TG, DTG and DTA curves of the SO_2–Co complex measured simultaneously in argon, heating rate 2 K min^{-1}, sample weight: 9.54 mg.

was determined by means of the DTA curve (damping of the exothermic reaction). The weight loss above 250°C belongs to the continuous decomposition of the complex.

Figure 2 shows the investigation of the SO_2–Co complex in N_2. The thermoanalytical curve is almost identical with the one in air. The weight loss of step 1 is 3.5%, which is slightly smaller due to the necessary atmosphere change (air 730 torr → 0.1 torr → N_2 730 torr). The decomposition reaction step 2 of 26.4% in the temperature range 100–250°C is exothermic regardless of the inert gas atmosphere. The oxidizing air atmosphere (Fig. 1) therefore does not influence the thermal decomposition of the SO_2–Co complex up to 350°C. The exothermic heat of reaction is probably caused by the SO_2/NH_3 separation or a secondary reaction between SO_2 and NH_3. The speculation that O_2 would be bound to the complex after the SO_2 and H_2O separations at higher temperatures is not confirmed, due to the fact that weight step 2 is equal to that in N_2. Neither a slight bond of O_2 nor of N_2 with the SO_2-free and H_2O-free Co complexes at room temperature can be excluded.

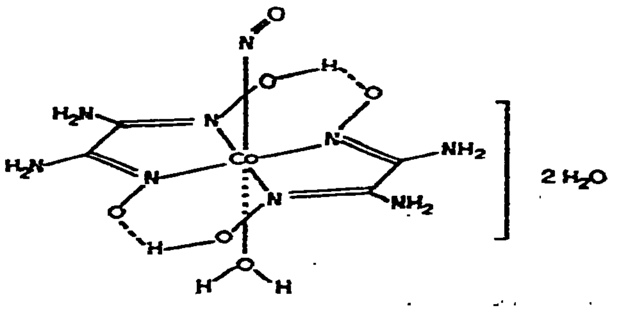
Figure 3 shows the investigation of this complex in argon; there are obviously no differences compared with the tests in air and N_2. The crystal water release, represented by step 1 of 1.8% (slightly smaller due to the atmosphere change), occurs in the temperature range 25–100°C. The exothermic decomposition reaction of 26.9% occurs in the temperature range of 100–250°C. Weight step 2 shows that neither O_2 nor N_2 are bonded after the separation of SO_2. The NH_3 separation from the Co complex (1) can be explained as follows, and leads to a diimine (2).



(1) (2)

The calculated weight loss for step 2 (SO_2 + H_2O + $2NH_3$) is 28.2%, which is well compatible with the values found (26.4–27.6%). The further thermal decomposition of the diimine complex (2) occurs above 250°C and leads, in an oxidizing atmosphere at 600°C, (as a residue) to Co_2O_3.

NO–Co complex



The investigation of $[(C_4H_{12}N_9O_6)Co] \cdot 2H_2O$ in air (Fig. 4) shows three

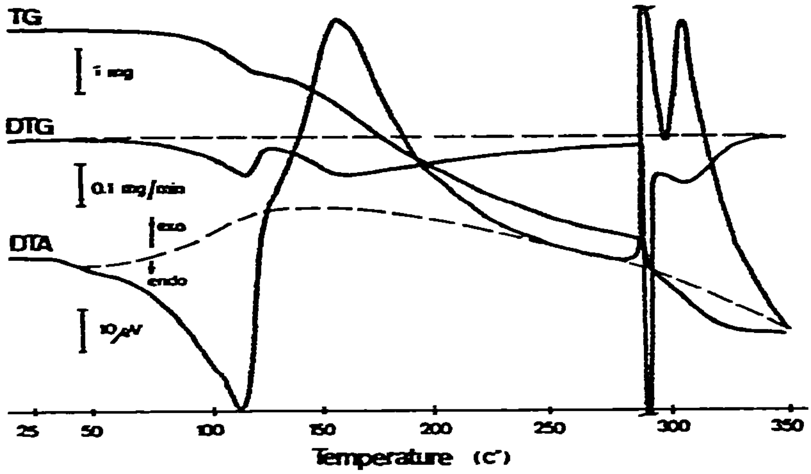


Fig. 4. TG, DTG and DTA curves of the NO–Co complex measured simultaneously in air, heating rate 2 K min^{-1}, sample weight: 9.81 mg.

TABLE 4

TG, DTA AND TEMPERATURE DETAILS FOR THE DECOMPOSITION OF THE NO–Co COMPLEX IN DIFFERENT ATMOSPHERES UP TO 350°C

Atmosphere	*Weight loss, step 1*			*Weight loss, step 2*		
	Temp. range (°C)	*DTA*	*%*	*Temp. range (°C)*	*DTA*	*%*
Synth. air	25–120	Endo	11.5	120–250	Exo	34.6
N_2	40–120	Endo	9.4	120–250	Exo	35.0
Argon	50–125	Endo	10.4	125–250	Exo	34.7

weight steps between 25–350°C. Among those steps, steps 1 and 2 are as important as in the SO_2–Co complex. Another interesting point is that the thermoanalytical curve is similar to those of the SO_2–Co complex taken in air, nitrogen and argon. Step 1 between 25–120°C which corresponds to a weight loss of 11.5% (Table 4) indicates that two molecules of crystal water are separated (the theoretical value is 9.6%). The exothermic weight step 2 between 120–250°C which shows a weight loss of 34.6% corresponds to the release of NO, coordinately bonded water, NH_3 and some other unknown decomposition products. The theoretically calculated value is 21.7%. This is caused because the complex which now does not contain NO has undergone a partial thermic dissociation. Only in air does a third weight step of 23.5% between 290–350°C occur caused by the influence of oxygen (strong exothermic reaction).

Figure 5 shows the NO–Co complex investigated in N_2 atmosphere. Although the gas atmospheres have been changed, weight step 1 between 40–120°C is about 9.4%. As a result of this observation we understand that the crystal water is tightly

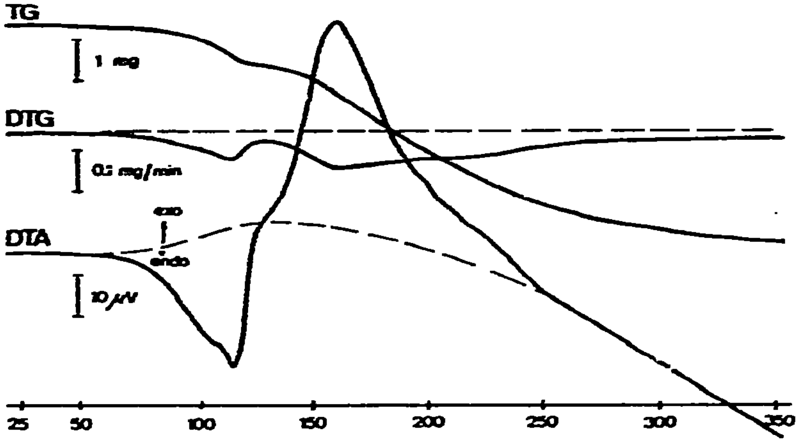


Fig. 5. TG, DTG and DTA curves of the NO–Co complex measured simultaneously in nitrogen, heating rate 2 K min^{-1}, sample weight: 9.56 mg.

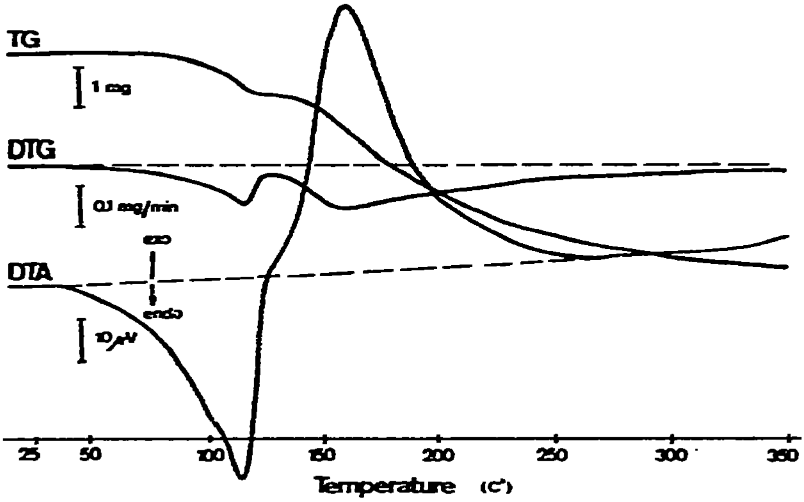


Fig. 6. TG, DTG and DTA curves of the NO–Co complex measured simultaneously in argon, heating rate 2 K min^{-1}, sample weight: 9.62 mg.

bonded to the NO–Co complex as is the case in the SO_2–Co complex. The weight loss step 2 of 35.0% between 120–250 °C is equal to that in air.

The thermoanalytical curve (Fig. 6) carried out in argon is similar to those taken in air and nitrogen. Considering that complex, the separation of crystal water, NO and coordinately bonded water is independent of the gas atmospheres. Step 1 between 50–125 °C shows a weight loss of 10.4% and step 2 between 125–250 °C of 34.7%, which is similar to those in the air and nitrogen.

CONCLUSIONS

The thermal decomposition of the SO_2–Co complex and the NO–Co complex was analyzed in air, N_2 and argon. It was found that the thermal decomposition of both complexes up to 350°C occurs in the same way, regardless of the atmosphere, resulting in very similar thermoanalytical curves (fingerprint).

The crystal water release of the SO_2–Co complex occurs in the temperature range 25–100°C, followed by the separation of SO_2, coordinately bonded H_2O and NH_3 (exothermic reaction) in the temperature range 100–250°C.

The crystal water release of the NO–Co complex occurs in the temperature range 25–125°C, followed by the separation of NO, H_2O and NH_3 as well as other unknown fractions (exothermic reaction) in the temperature range 125–250°C.

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