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ON THE DIOXIMINE COMPLEXES OF TRANSITION METALS

LXXVII. Formation and thermal decomposition of some complexes $NH_4[Co(DH)_2(SO_3)(amine)] \cdot tH_2O$

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Twelve new complexes $NH_4[Co(DH)_2(SO_3)(amine)] \cdot tH_2O$ (DH_2 = dimethylglyoxime) have been synthesized and characterized. Their i.r. spectra show the SO_3 to be co-ordinated to the Co atom through the S atom. The thermal decompositions of a series of derivatives of this type have been investigated with a derivatograph. The first process is an endothermic dehydration reaction, occurring in a single stage or in two successive ones. The loss of the crystallization water is followed by another endothermic reaction, without a clear stoichiometry, which is referred to as "deamination". At higher temperatures, exothermic pyrolysis processes occur. From the TG curves, kinetic parameters have been derived for the dehydration and deamination reactions.

The sulfito group (SO_3^{2-}), an ambidentate ligand, can be co-ordinated to metal ions through either the oxygen or the sulfur atom. The number of reported sulfito complexes with M—O—SO_2 bonding is small: $Tl_2[Cu(SO_3)_2]$ [1], $Na_8[Os(SO_3)_6] \cdot 8H_2O$ [2], $[Cr(SO_3)_2]^-$ [3], $[UO_2(SO_3)_2]^{2-}$ [4] and $[NpO_2(SO_3)_2]^-$ [5].

In the sulfito complexes of most transition metals the co-ordination of this group occurs through the sulfur atom: e.g. $[Ir(NH_3)_4(SO_3)_2]^-$, $[Ir(en)_2Cl(SO_3)]$ [6], $[Rh(NH_3)_2(SO_3)_4]^{5-}$ [7], $[Co(NH_3)_5(SO_3)]^+$ [8], $[Co(en)_2(SO_3)_2]^-$ [9], $[Co(SO_3)(CN)_5]^{4-}$ [10].

In the present paper the synthesis and characterization of some complexes $NH_4Co(DH)_2(SO_3)X$ is described, where DH_2 stands for dimethylglyoxime, and X for amines or other neutral molecules.

A derivatographic study of the thermal decomposition of the complexes obtained has been performed, as a continuation of our previous investigations concerning the thermal decomposition of complexes $M[Co(DH)_2(SO_3)X]$ (M = Na, K) [11].

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Synthesis of complexes $NH_4[Co(DH)_2(SO_3)X]$

The sulfito group can easily be introduced into the inner coordination sphere of the dioximinocobalt(III) derivatives. The substitution reactions of $[Co(Diox.H)_2(H_2O)_2]^+$, $[Co(Diox.H)_2(H_2O)Cl]$ and $[Co(Diox.H)_2(NH_3)_2]^+$ ($Diox.H_2$ = various α-dioximes) with Na_2SO_3 leads to the formation of $Na_3[Co(Diox.H)_2(SO_3)_2]$ [12]. In these compounds one of the sulfito groups can readily be replaced by a water molecule. The sulfito-aquo complexes obtained $[Co(Diox.H)_2(SO_3)(H_2O)]^-$ are good starting materials for the synthesis of various derivatives by anation reactions with halides and pseudohalides. The water molecule can be substituted by other neutral molecules, such as amines, *N*-bases, phosphines, arsines, etc. Since the sulfito group has the greatest trans-effect after the cyanide ion, it is not exchanged during the above substitution reactions. Thus, the products obtained are very pure.

Some derivatives $M[Co(DH)_2X(SO_3)]$ with X = Cl, Br, I, NO_2, NCS, urea, thiourea, thioacetamide, etc. have already been obtained and characterized [13, 14]. For the synthesis of analogous derivatives, besides dimethylglyoxime, monomethylglyoxime [15] and α-benzyldioxime [16] have been used.

In the present paper, 12 new complex salts of the type $NH_4[Co(DH)_2(SO_3)(amine)] \cdot tH_2O$ were obtained by means of anation reactions of $NH_4[Co(DH)_2(SO_3)(H_2O)]$ with different aromatic amines and heterocyclic N-bases. The aromatic amines with pK_b values between 9 and 13 were observed to coordinate easily to the $Co(DH)_2$ nucleus:

$$[Co(DH)_2(SO_3)(H_2O)]^- + amine = [Co(DH)_2(SO_3)(amine)]^- + \\ + H_2O$$

The very weak bases ($pK_b > 14$) (e.g. nitroanilines, nitrotoluidines, nitroethylanilines, sulfanilic and anthranilic acids) are not suitable for this purpose.

The new complex salts obtained are characterized in Table 1.

I.R. Spectra

The i.r. spectra of the sulfitodimethylglyoximino complexes show the Co—SO_3 bonding to be formed through the sulfur atom.

The SO_3 ligand, as others of XY_3 type, has a pyramidal structure, giving C_{3v} site symmetry, taking all these complexes as R—SO_3-type molecules. The four characteristic vibration bands of the free SO_3^{2-} ion appear in both the i.r. and the Raman spectra of all the sulfito complexes. The co-ordination of SO_3^{2-} through the sulfur atom leads to a diminution of the negative charge of the oxygen atoms and to an increase of the bonding order of the S—O bond. Thus, the frequencies of the

Table 1 New $NH_4[Co(DH)_2(SO_3)(amine)] \cdot tH_2O$ type complexes

No.	Formula	Mol. wt., calcd.	Aspect	Analysis	calcd., %	found, %
1	$NH_4[Co(DH)_2(SO_3)(m\text{-}anisidine)_2] \cdot 4H_2O$	582.5	sparkling, yellow prisms	Co	10.11	10.15
				S	5.50	5.55
				H_2O	12.37	12.56
2	$NH_4[Co(DH)_2(SO_3)(2,4\text{-}dimethoxy\text{-}aniline)] \cdot 4H_2O$	612.5	yellow irregular prisms	Co	9.62	9.80
				S	5.24	5.42
				H_2O	11.76	11.58
3	$NH_4[Co(DH)_2(SO_3)(benzylamine)] \cdot H_2O$	512.3	short, yellow prisms	Co	11.50	11.40
				H_2O	3.51	3.60
4	$NH_4[Co(DH)_2(SO_3)(m\text{-}amino\text{-}fenol)] \cdot 4H_2O$	568.5	dark yellow plates	Co	10.37	10.25
				S	5.64	5.60
5	$NH_4[Co(DH)_2(SO_3)(imidazole)] \cdot H_2O$	473.3	yellow-brown plates	Co	12.45	12.60
				S	6.77	6.60
6	$NH_4[Co(DH)_2(3\text{-}ethyl\text{-}pyridine)(SO_3)]$	494.4	yellow-brown square prisms	Co	11.92	11.80
				S	6.48	6.76
7	$NH_4[Co(DH)_2(SO_3)(4\text{-}ethyl\text{-}pyridine)]$	494.4	yellow-brown square prisms	Co	11.92	11.73
				S	6.48	6.29
8	$NH_4[Co(DH)_2(3,4\text{-}lutidine)(SO_3)] \cdot H_2O$	512.4	yellow square prisms	Co	11.50	11.33
				S	6.27	6.45
				H_2O	3.52	3.60
9	$NH_4[Co(DH)_2(SO_3)(3,5\text{-}lutidine)]$	494.4	rhombohedral yellow plates	Co	11.92	11.80
				S	6.48	6.60
10	$NH_4[Co(DH)_2(SO_3)(m\text{-}Br\text{-}aniline)] \cdot 4H_2O$	631.3	brown plates	Co	9.33	9.25
				S	5.07	5.13
				H_2O	11.41	11.60
11	$NH_4[Co(DH)_2(SO_3)(o\text{-}I.\ aniline)] \cdot 4H_2O$	678.3	yellow needles	Co	8.69	8.45
				S	4.73	4.84
				H_2O	10.02	10.15
12	$NH_4[Co(DH)_2(SO_3)(p\text{-}xylidine)] \cdot 4H_2O$	580.4	sparkling, brown rhomb. plates	Co	10.14	10.10
				H_2O	12.42	12.16

Co content detn. complexometrically, S as $BaSO_4$

symmetrical valence vibration ν_s, and especially that of the double degenerated asymmetric valence vibration, are increased as compared to the values of $\nu_s = 960$–$970\ cm^{-1}$ and $\nu_{as} = 930$–$950\ cm^{-1}$ for the free SO_3^{2-} ion. For the sulfito complexes of Co(III), Ir(III), Rh(III) and Pt(III), they are situated at about $\nu_s = 960$–1010 and $\nu_{as} = 1020$–$1175\ cm^{-1}$. The bending vibrations δ_s appear in approximately the same interval ($\delta_s = 610$–$680\ cm^{-1}$) as for the free ion

616–655 cm^{-1}. The asymmetrical bending vibration is shifted a little towards higher wavenumbers (δ_{as} = 500–560 cm^{-1}) as compared to the value (δ_{as} = 445–530 cm^{-1}) for the free sulfite ion [16].

In the case of the bis-dimethylglyoximato-Co(III) complexes, the exact assignment of ν_{as} and δ_{as} is rather difficult, due to the strong valence vibration of the N—O bond of the oxime, situated at about 1050–1150 cm^{-1}, which is sometimes partially overlapped by the strong ν_{as} vibration of the S—O bond, and to the ν_{Co-N} vibration at about 500–530 cm^{-1}, partially overlapped by the δ_{as} vibration of the S—O bond. The presence of these vibrations is observed in the i.r. spectra of all the complexes studied in the present paper, showing that they are all sulfito complexes with SO_3 ligands linked to the Co atom through the sulfur atom.

The i.r. spectra reveal the presence of strong intramolecular O—H. . O hydrogen-bonds (ν_{O-H}: 2350–2400 cm^{-1} (w), $\nu_{O-H..O}$ 1700–1800 cm^{-1} (vw)), similar to those observed with the other bisdimethylglyoximato-Co(III) complexes, as $H[Co(DH)_2X_2]$ or $[Co(DH)_2(amine)_2]X$. These hydrogen-bonds stabilize the coplanar $Co(DH)_2$ ring system, i.e. the trans configuration of the complexes of the above type [17].

The characteristic vibrations of the co-ordinated oxime groups have been found to be $\nu_{C=N}$: 1570–1580 cm^{-1} (s), ν_{N-O} = 1240 cm^{-1} (s) and 1090–1100 cm^{-1} (s) partially overlapped by ν_{as}(S—O).

The ν_{N-H} stretching vibrations of the co-ordinated aromatic amines appear at 3200 and 3150 cm^{-1}, shifted by 200–250 cm^{-1} towards lower values as compared to the free, non-bonded amines. The Co—N(amine) bond has a strong covalent character.

Electronic spectra

In the electronic spectra of the complexes studied, no clear crystal field transitions can be observed. All these complexes have two strong charge-transfer bands at about 33–34 and 41–42 kK, as the other bis-dimethylglyoximato-Co(III) complexes [18].

The positions of these bands seem to be influenced by the nature of the ligand X occupying the position trans to the SO_3 group. Both bands are shifted towards higher wavenumbers if the ligand X can form relatively strong π-bonds with the Co atom. Thus, for X = NCSe, or thiourea, the mean wavenumbers of these bonds are higher as compared to those for 10 other analogous complexes, where the formation of Co—X π-bonds is impossible, or these bonds are very weak [11]. This effect allows the assumption that these bands are Co→DH charge-transfer bands.

Thermal decomposition

The thermal decomposition of the complexes $NH_4[Co(DH)_2(SO_3)X]$ was studied under dynamic temperature conditions with a derivatograph.

The substances studied are crystallohydrates. Loss of the crystallization water molecules occurs between 50 and about 130°. In the TG curve, one or two weight loss stops appear, corresponding to the end of these dehydration processes, with the same number of endotherms in the DTA curves.

The thermal decomposition of the anhydrous complexes is a more complicated process than with the complexes $[Co(DH)_2(amine)_2]X$ investigated previously [19, 20].

In the latter case a stoichiometric partial deamination process was observed as the first stage of the pyrolysis, corresponding to the reaction

$$[Co(DH)_2(amine)_2]X = [Co(DH)_2(amine)X] + amine$$

In the case of the sulfito complexes studied previously [11], the dehydration was generally followed by a complex exothermal process, leading to the total destruction of the co-ordination sphere, without the formation of a relatively stable, well-defined intermediate. For the ammonium salts studied in the present paper, after the dehydration processes another endothermal reaction occurs, which will be referred to as deamination, but it does not lead to a well-defined intermediate. The further decomposition stages are complex exothermal reactions, presumably with the participation of atmospheric oxygen and imply the destruction of the whole co-ordination sphere. Some illustrative DTA and TG curves are given in Fig. 1.

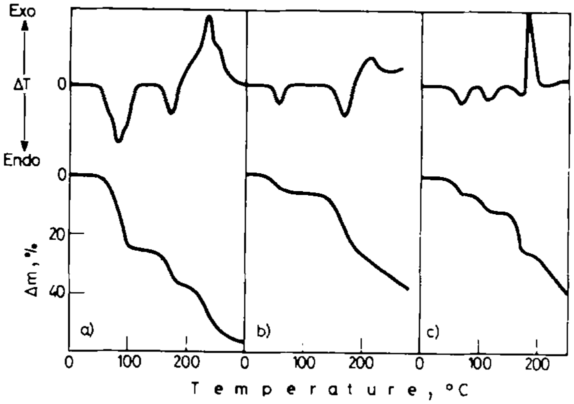

Fig. 1 DTA and TG curves. *a)* $NH_4[Co(DH)_2(SO_3)(H_2O)] \cdot 8H_2O$; *b)* $NH_4[Co(DH)_2(SO_3)$(*N*-diethylaniline)$] \cdot 2H_2O$; *c)* $NH_4[Co(DH)_2(SO_3)$(α-naphthylamine)$] \cdot 4H_2O$

The pyrolysis of $NH_4[Co(DH)_2(SO_3)(H_2O)] \cdot 8H_2O$ (Fig. 1a) begins with the loss of the crystallization water. This apparently occurs in a single stage, although the asymmetry of the DTA peak shows the overlap of at least two successive stages. The deamination is marked by a DTA endotherm and by a weight loss, leading to a not well-defined intermediate. The further decomposition is an exothermal process, presumably with the participation of atmospheric oxygen.

For $NH_4[Co(DH)_2(SO_3)(\text{N-diethylaniline})] \cdot 2H_2O$ (Fig. 1b) the dehydration also occurs in a single stage. The endothermal deamination is followed by an exothermal process.

$NH_4[Co(DH)_2(SO_3)(\alpha\text{-naphthylamine})] \cdot 4H_2O$ loses its crystallization water in two stages (Fig. 1c), indicated by two DTA endotherms and two weight loss stops in the TG curve. The endothermal deamination leads to an appreciable weight loss, but it is followed immediately by another reaction with a strong exothermal effect, but practically no weight loss.

The characteristics of the decomposition reactions are presented in Table 2.

Table 2 Thermal characteristics of the decomposition reactions of $NH_4[Co(DH)_2(SO_3)X] \cdot tH_2O$ type complexes

X	t	q deg/min	DTA peak temperatures						Temp. range investigated °C
			endothermic			exothermic			
			dehydration		deamination	dehydration		deamination	
H_2O	8	5	80		172	230	340		20–500
NH_3	1	3	85		173	185			20 250
pyridine	3	3	95		120	220			20–250
β-picoline	3	3	85	110		195			20–250
aniline	4	3	80	118	185	215			20 250
o-toluidine	4	3	75	100	165	188	235		20–250
p-toluidine	4	3	72	118	168	215	245		20–250
o-ethyl-aniline	2	3	60		143	235			20–250
N-diethylaniline	2	3	65		171	210			20–250
o-anisidine	2	3	100		155	245			20–250
m-anisidine	4	10	90		180	—			20 250
p-anisidine	4	3	76	120	168	175			20–250
2,4-dimethoxy-aniline	4	10	85		184	220			20 250
m-amino-fenol	4	10	85	125	210	—			20–250
α-naphthylamine	4	3	68	110	166	177			20–250
β-naphthylamine	4	3	74	109	173	188			20–250
imidazole	1	20	120		190	300	415		20–1000
urea	4	3	110		160	205	310	450	20–500
thiourea	2	3	72		148	200	260	355	20–500
allylthiourea	1	3	60		170	188	248		20–500

Deriving of kinetic parameters

The shape of the TG curves allowed us in several cases to derive kinetic parameters for the endothermal decomposition stages from the TG curves. These kinetic parameters, the apparent reaction order n, the activation energy E and $\log Z$, were calculated by using a computerized variant of the Coats–Redfern method [22]. Z values were obtained by expressing the heating rate q in $K\,s^{-1}$. Kinetic parameters and the temperature values $T_{0.1}$ at which the transformation degree in the decomposition stage considered is equal to $\alpha=0.1$ are given in Tables 3–5 for the different decomposition stages.

As seen from Table 3, the first dehydration begins at very low temperatures and the apparent activation energy is small. The E and $\log Z$ values vary in parallel due

Table 3 Kinetic parameters for the first dehydration stage

X	n	E, kJ	$\log Z$	$T_{0.1}$, °C
H_2O	1.50	92.5	11.2	61
NH_3	1.78	55.6	5.7	47
pyridine	0.87	44.0	3.4	57
β-picoline	0.39	54.3	5.4	48
aniline	0.37	58.6	6.3	45
o-toluidine	1.50	67.3	7.5	52
p-toluidine	1.28	123	16.9	48
o-ethyl-aniline	2.97	106	14.4	47
N-diethylaniline	0.83	106	14.6	38
o-anisidine	0.80	33.1	1.7	55
p-anisidine	0.84	75.7	8.9	50
α-naphthylamine	0.97	94.7	12.4	44
β-naphthylamine	0.80	85.7	10.6	48
urea	0.77	53.6	5.6	70
thiourea	0.75	109	14.6	49
allylthiourea	0.64	30.5	1.2	59

Table 4 Kinetic parameters for the second dehydration stage

X	n	E, kJ	$\log Z$	$T_{0.1}$, °C
β-picoline	2.97	402	54.3	100
aniline	1.14	98.4	11.0	88
p-toluidine	0.39	81.7	8.6	85
p-anisidine	1.72	165	19.9	101
α-naphthylamine	1.11	122	14.7	82
β-naphthylamine	1.16	155	19.6	86

Table 5 Kinetic parameters for the endothermal deamination stage

X	n	E, kJ	$\log Z$	$T_{0.1}$, °C
H_2O	0.42	131	12.8	150
NH_3	0.17	140	13.8	154
β-picoline	0.98	247	26.4	164
aniline	0.87	277	29.5	172
o-toluidine	0.83	108	9.6	160
p-toluidine	1.03	271	29.9	157
o-ethyl-aniline	1.33	278	33.0	132
N-diethyl-aniline	0.81	138	13 9	148
o-anisidine	1.16	92.1	8.1	147
p-anisidine	0.84	311	34.9	156
α-naphthylamine	1.11	326	36.3	163
β-naphthylamine	1.58	312	33.6	172

to the kinetic compensation effect [23]. The plot of $\log Z$ *vs.* E gives a good linearization, showing the validity of a kinetic compensation law

$$\log Z = aE+b$$

With the kinetic parameters given in Tables 3–5, the plot of $\log Z$ *vs.* E gives two straight lines: one for the dehydration and the other for the deamination process. The corresponding kinetic compensation parameters a and b, calculated by means of the least square method, are given in Table 6, together with Jaffé's correlation coefficient ϱ [24], indicating a very good linearity.

The compensation parameter a found for the dehydration reactions is very close to those obtained for other dehydration processes, e.g. the dehydration of some dithionates [25], complexes $[M(en)_3]X_{3.tH_2O}$ [26] and $M[Co(DH)_2(SO_3)X]\cdot tH_2O$ [11]. It is worth mentioning that the $\log Z$ *vs.* E pairs reported previously [11] are situated on practically the same straight line as the kinetic parameters of the dehydration reported in the present paper. The kinetic compensation parameters calculated from all the kinetic parameters given in Tables 3 and 4 and reported earlier [11] for the dehydration of other sulfito-dimethylglyoximino-Co(III) complexes, are given in the same Table 6 as DHy+ (11).

They are sec to be almost identical with those obtained only for the ammonium salts DHy and even the correlation coefficients are exactly as good in the two cases.

The kinetic parameters of the deamination reaction do not give the same straight line as those of the dehydration. This can be seen from the correlation coefficient obtained for the plot of all $\log Z$ *vs.* E pairs given in Tables 3–5 (DHy + DA in Table 6), which is significantly less than the correlation coefficients obtained separately for the dehydration and deamination reactions.

Fig. 6 Kinetic compensation parameters for the different decomposition stages

Stage	a, mole/kJ	b	ϱ	a'
dehydration (DHy)	0.141	−2.01	0.997	0.156
deamination (DA)	0.121	−3.12	0.997	0.122
DHy+(11)	0.142	−2.06	0.997	0.157
DHy+DA	0.120	−0.91	0.984	0.142

According to Garn [27], the compensation parameter a is correlated to the "decomposition temperature" T_c:

$$a = 1/2.3\,RT_c$$

With T_c taken as the arithmetical mean of the $T_{0.1}$ values given in Tables 3–5 (and also in [11] in the variant DHy+(11)), a values were calculated by means of the above relation. They are given in Table 6 as a'.

The a and a' values are almost identical for the deamination reaction, in agreement with Garn's hypothesis, but they are rather different for the dehydration reactions. This disagreement between a and a', as well as the almost identical a value obtained for the loss of crystallization water linked to alkali metal, ammonium and alkaline earth metal cations [11, 25] or to simple anions [26], seems to support our hypothesis [26] that the parameter a is a measure of the strength of the bond broken in the thermal decomposition, i.e. the stronger the bond, the lower the a value.

Experimental

$NH_4[Co(DH)_2(SO_3)(H_2O)]\cdot 9H_2O$. 100 mmol 35 g $[Co(DH)_2Cl(H_2O)]$ prepared by boiling $H[Co(DH)_2Cl_2]$ in water in 200 ml aqueous suspension is treated with stoichiometric freshly-prepared $(NH_4)_2(SO_3)\cdot H_2O$ (12 g) in 25 ml water. The chloro-aquo nonelectrolyte dissolves slowly and the aquo-sulfito ammonium salt crystallized after 6–10 hr standing as sparkling, large, brown prisms. Yield: 75%. Analysis: Co calcd. 10.38, found 10.42; S calcd. 5.65, found 5.50.

$NH_4[Co(DH)_2(SO_3)(amine)]\cdot H_2O$ salts. 10 mmol $NH_4[CO(DH)_2(SO_3)(H_2O)]\cdot 9H_2O$ is dissolved in 20–25 ml water and treated with 5–10 mmol of the corresponding amine in 10–15 ml alcohol. The mixture is kept on a water-bath for 30–40 min. The sulfito-amino salt formed is separated with excess acetone.

Purification: The crude product is dissolved in a small amount of water, filtered and reprecipitated with acetone.

IR spectra were recorded in KBr pellets with a UR 20 Carl Zeiss spectrophotometer. Electronic spectra were obtained in aqueous solutions with a Specol (Carl Zeiss, Jena) spectrophotometer.

The derivatographic measurements were made with a MOM derivatograph [27]. Sample weight: 100 mg. Atmosphere: static air. Reference material: α-Al_2O_3. Platinum crucible.

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Zusammenfassung — Zwölf neue Komplexe der allgemeinen Formel $NH_4[Co(DH)_2(SO_3)(amin)] \cdot tH_2O$ (*DH* = Dimethylglyoxim) wurden synthetisiert und charakterisiert. Die IR-Spektren zeigen, daß SO_3 über das S-Atom koordinativ an das Co-Atom gebunden ist. Die thermische Zersetzung einer Reihe von Derivaten dieses Typs wurde mittels eines Derivatographen untersucht. Der erste Prozeß ist die in einem einzigen oder in zwei aufeinander folgenden Schritten verlaufende endotherme Dehydratisierung. Auf die Abgabe des Kristallwassers folgt eine andere endotherme Reaktion unklarer Stöchiometrie, die als „Deaminierung“ bezeichnet wird. Bei höheren Temperaturen verlaufen exotherme Pyrolyseprozesse. Aus den TG-Kurven wurden kinetische Parameter für die Dehydratisierung und die Deaminierung bestimmt.

Резюме — Синтезированы и охарактеризованы двенадцать новых комплексов $NH_4[Co(DH)_2(SO_3)(\text{амин})] \cdot tH_2O$, где DH_2 — диметилглиоксим. ИК спектры показали, что сульфито группа координируется с атомом кобальта через серу. Термическое разложение комплексов исследовано с помощью дериватографа. Первоначальным процессом разложения является эндотермическая реакция дегидратации, проходящая в одну стадию или в две последовательных стадии. Потеря кристаллизационной воды сопровождается другой эндотермической реакцией с неопределенной стехиометрией и которая обозначена как реакция «деаминирования». При более высоких температурах происходят экзотермические процессы пиролиза. На основе кривых ТГ установлены кинетические параметры реакций дегидратации и деаминирования.