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STRUCTURAL AND THERMAL ANALYSIS OF BIS-(5-SULPHOSALICYLATO)-DIAQUO COMPLEXES OF VO(II), Cu(II), Ni(II), Co(II), Fe(II) AND Mn(II)

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The reactions of the 5-sulphosalicylate anion with VO(II), Cu(II), Ni(II), Co(II), Fe(II) and Mn(II) gave bis-(5-sulphosalicylato)–diaquo complexes. The structures of these complexes were predicted from elemental analyses and IR spectra. Their decompositions were studied by TG, DTG and DTA. Decomposition occurred in two steps: elimination of two water molecules, followed by decomposition of the dehydrated complex to give metal oxide as end-product. The thermal stability sequence for the complexes was

$$\mathrm{VO(II)} > \mathrm{Cu(II)} > \mathrm{Co(II)} \approx \mathrm{Ni(II)} \approx \mathrm{Fe(II)} > \mathrm{Mn(II)},$$

which is in accordance with the covalency sequence for the M–O bond.

The thermal decomposition of metal complexes with chelating organic ligands has attracted great interest during recent years. However, work on the thermal decomposition of metal chelates of salicylic and nuclear-substituted salicylic acids started only a short time ago. The decarboxylation and thermal stability of salicylic acid (SA) [1] and 4-aminosalicylic acid (4ASA) and their sodium and calcium salts have been investigated [2], but little is known about these features of other metal salicylates [3–9]. We are interested in the thermal study of the complexes of transition metals with salicylic acids, for we have already investigated the antimicrobial activities of these complexes [10–14]. As an extension of our previous work [15–19], the present paper report deals with the thermal decomposition of metal chelates of VO(II), Cu(II), Ni(II), Co(II), Fe(II) and Mn(II) with 5-sulphosalicylic acid (5SSA). The study has provided valuable information about their dehydration, the pyrolysis of the anhydrous complexes and the intermediates during their decomposition, which will facilitate the synthesis of analogous biologically active complexes.

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Experimental

Materials and methods

The complexes were prepared by the method described previously [20]. Equimolar solutions of metal salts and the ligand were prepared and mixed in the stoichiometric ratio $M:L = 1:2$. The solid complexes obtained were washed thoroughly with ethanol, dried and recrystallized from dimethylformamide. All the reagents used were of BDH AnalaR grade. Metal contents were estimated by conventional methods [21]. Elemental analyses (carbon and hydrogen) were carried out in the usual way. The bonding in the complexes was established by IR spectral study.

Instrumental

Elemental analyses

Metal contents were determined by the conventional methods [21]. Carbon and hydrogen analyses were carried out with a Colemann 29 CHN analyser.

IR spectra

IR spectra of all the bis-(5-sulphosalicylato)–diaquo complexes and their dehydrated products were recorded on KBr discs with a Perkin–Elmer 377 grating IR spectrophotometer. The IR spectrum of the ligand was also recorded for comparison. The region 4000–400 cm^{-1} was scanned in 13 minutes.

Far IR spectra were recorded in the region 500–50 cm^{-1} with a Polytec FIR 30 Fourier far IR spectrometer.

Thermogravimetry

TG was carried out in air on a Stanton HT thermobalance at 1 mg sensitivity, with a heating rate of 4 deg/min. The chart speed was maintained at 3 inches/hr. All the samples were of the same particle size and were packed as uniformly as possible in a platinum crucible of appropriate size. The same platinum crucible was used throughout the experiments.

Differential thermal analysis

The DTA assembly with temperature programmer of F and M Scientific Hewlett–Packard and a platinel II thermocouple of Engelhard (U. S. A.) were used. DTA curves were recorded with a Rikadenki Kogyo recorder in static air at a heating rate of 4 deg/min. Alumina was used as a reference standard.

Results and discussion

Analytical data on the complexes are presented in Table 1. TG, DTG and DTA curves are shown in Figs 1–3, while the corresponding transition temperatures, TG weight loss data and DTA peak temperatures are listed in Tables 2 and 4. The positions of the characteristic IR bands are shown in Table 2.

Table 1 Analytical data on the bis-(5-sulphosalicylato)–diaquo complexes and their dehydrated products

Complex	Colour	M%		C%		H%	
		Calc.	Found	Calc.	Found	Calc.	Found
$Cu(5SSA)_2 \cdot 2\,H_2O$	green	11.95	12.25	31.60	30.98	2.25	2.31
$Cu(5SSA)_2$ (dp)	dark-green	12.76	12.82	33.77	34.00	2.01	1.92
$Ni(5SSA)_2 \cdot 2\,H_2O$	light-green	11.14	11.82	31.89	31.27	2.28	2.20
$Ni(5SSA)_2$ (dp)	green	11.92	12.00	34.09	33.87	2.03	2.10
$Co(5SSA)_2 \cdot 2\,H_2O$	pink	11.18	10.98	31.88	31.16	2.27	2.34
$Co(5SSA)_2$ (dp)	brown	11.95	12.02	34.08	34.12	2.03	2.09
$Mn(5SSA)_2 \cdot 2\,H_2O$	light-buff	10.50	10.41	32.12	31.89	2.29	2.21
$Mn(5SSA)_2$ (dp)	tan	11.23	11.15	34.37	34.10	2.05	2.13
$Fe(5SSA)_2 \cdot 2\,H_2O$	coffee-coloured	10.66	11.04	32.07	31.92	2.29	2.23
$Fe(5SSA)_2$ (dp)	dark-brown	11.40	11.36	35.10	35.22	2.04	2.14
$VO(5SSA)_2 \cdot 2\,H_2O$	dark-green	12.51	12.41	31.4	32.08	2.24	2.20
$VO(5SSA)_2$ (dp)	bright-green	13.36	13.42	33.54	33.62	2.00	1.92

dp = decomposition product.

Stoichiometry and structure of the complexes

The analytical data in Table 1 indicate that all these complexes have stoichiometry $ML_2 \cdot 2\,H_2O$, where M is VO(II), Cu(II), Ni(II), Co(II), Fe(II) or Mn(II), and L is the anion of 5SSA.

The IR spectrum of solid 5SSA is almost identical to that of its complexes in the region 2000–600 cm^{-1}. The frequencies of most interest with regard to structure are those of the C–O and O–H vibrations. The $\nu(C=O)$ band at 1665 cm^{-1} is shifted to a lower frequency ($\approx$ 1630 cm^{-1}) in all the complexes, showing that complexation has taken place through the carboxyl group [22, 23]. The appearance of a new band in the vicinity of 840 cm^{-1} for all the complexes demonstrates water coordinated to the metal ion [24–26]. A band at $\approx$ 315 cm^{-1} confirms the presence of coordinated water [27]. The presence of coordinated water is borne out by the thermal decomposition data (Figs 1–3). The δO–H (phenolic) bending peak at 1350 cm^{-1} is at almost the same position in the spectra of 5SSA and its complexes. This shows that there is no loss of proton by the phenolic OH group upon coordination.

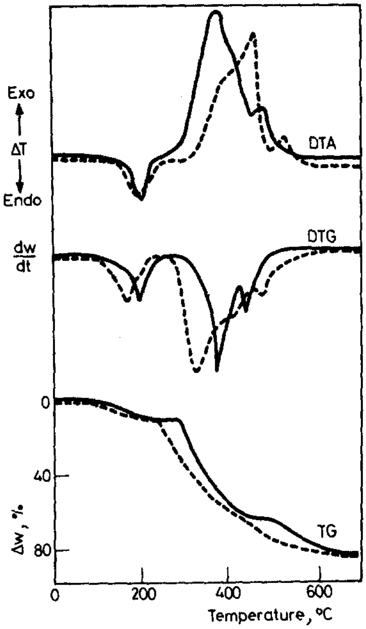

Fig. 1 TG, DTG and DTA curves for bis-(5-sulphosalicylato)–diaquo complexes. —— Cu(II), – – – Ni(II)

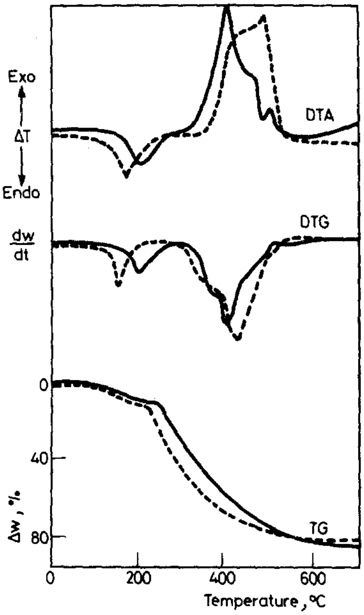

Fig. 2 TG, DTG and DTA curves for bis-(5-sulphosalicylato)–diaquo complexes. —— Co(II), – – – Mn(II)

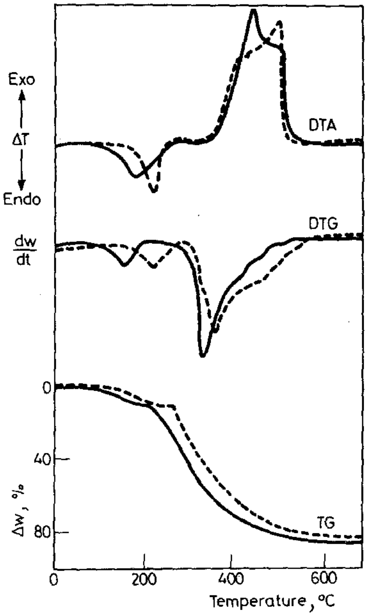

Fig. 3 TG, DTG and DTA curves for bis-(5-sulphosalicylato)–diaquo complexes. —— Fe(II), – – – VO(II)

Table 2 Characteristics IR frequencies for bis-(5-sulphosalicylato)–diaquo complexes

Assignment	5SSA	Cu(II)	Ni(II)	Co(II)	Mn(II)	Fe(II)	VO(II)
νCOO^- asym.	1665 (S)	1648 (S)	1650 (S)	1640 (S)	1630 (S)	1635 (S)	1650 (S)
νCOO^- sym.	1445 (S)	1420 (S)	1431 (S)	1430 (S)	1420 (S)	1425 (S)	1420 (S)
νO–H Str.	2400–3600 (3200) (Sb)	2800–3750 (3475) (Sb)	2900–3690 (3450) (Sb)	3000–3715 (3510) (Sb)	2900–3670 (3400) (Sb)	2700–3690 (3480) (Sb)	2800–3680 (3520) (Sb)
δO–H	1353 (S)	1341 (S)	1353 (S)	1353 (S)	1341 (S)	1352 (S)	1364 (S)
δH_2O rocking	–	850 (S)	842 (S)	832 (S)	830 (S)	822 (S)	872 (S)
ν(M–O) + (C–C)	–	530 (w)	520 (mb)	495 (w)	490 (Sh)	505 (m)	510 (w)
ν(M–O) + ring defor.	–	440 (Sb)	420 (w)	428 (m)	405 (Sh)	425 (w)	430 (Sh)
ΔC=O	–	228	219	210	210	210	230

S = strong, b = broad, w = weak, m = medium, Sh = shoulder.

Behaviour of the complexes

All the complexes are insoluble in water and common organic solvents, suggesting a polymeric structure for each of them. Their insolubility in common organic solvents meant that the extent of polymerization could not be determined. Earlier data on the magnetic susceptibility and electronic spectra indicated octahedral stereochemistry for all the complexes [28]. The thermal decomposition would appear to be consistent with this type of structure and would suggest that the water molecules are directly bonded to the metal ion, along with two 5SSA moieties, to give a coordination number of six for each of the metal(II) ions.

The increase in the difference between νCOO(asym) and νCOO(sym) ($\Delta C=O$) has been taken as a measure of increasing covalency of the M—O bond [29]. The 5SSA complexes presented a band at $\approx$ 1640 cm^{-1} (Table 2) for νCOO(asym) and at $\approx$ 1420 cm^{-1} for νCOO(sym). Thus, the covalent character of the M—O bond follows the sequence

$$Fe(II) < Mn(II) < Co(II) < Ni(II) < Cu(II) < VO(II)$$

Thermal decomposition

Thermal decomposition curves for all six isostructural complexes of 5SSA are given in Figs 1–3, while the TG weight loss data and DTA peak temperatures are to be found in Tables 3 and 4.

Table 3 Analytical data for the bis-(5-sulphosalicylato)--diaquo complexes[a]

Complex	D.P.[b]	Temperature range, °C	Colour	Composition of the residue	Weight loss, %W	
					Calc.	Obs.
(I) $Cu(5SSA)_2 \cdot 2\,H_2O$	I	100–240±4		$Cu(5SSA)_2$	6.77	6.50
	II	260–620±2	black	CuO	85–03	84–75
(II) $Ni(5SSA)_2 \cdot 2\,H_2O$	I	80–220±4		$Ni(5SSA)_2$	6.83	7.00
	II	230–580±3	greenish black	NiO	85.81	86.25
(III) $Co(5SSA)_2 \cdot 2\,H_2O$	I	100–230±3		$Co(5SSA)_2$	6.83	6.75
	II	250–600±2	dark brown	CoO	85.77	86.50
(IV) $Mn(5SSA)_2 \cdot 2\,H_2O$	I	80–210±3		$Mn(5SSA)_2$	6.88	7.00
	II	220–570±4	grey green	MnO[c]	86.43	85.00
(V) $Fe(5SSA)_2 \cdot 2\,H_2O$	I	90–210±4		$Fe(5SSA)_1$	6.87	6.50
	II	230–640±3	dark brown	FeO[d]	86.28	85.25
(VI) $VO(5SSA)_2 \cdot 2\,H_2O$	I	110–260±4		$VO(5SSA)_2$	6.72	6.25
	II	280–620±2	dark blue	O=V=O[e]	84.49	83.00

a = all the experiments were carried out in air at a heating rate of 4 °C/min, *b* D.P. = decomposition period (step), *c* = in the final residue, the possibility of formation of Mn_3O_4 can not be ruled out as the experiments were carried out in air, *d* = FeO was the major end product above 600 °C, however, below this temperature it gets contaminated with Fe_3O_4, as the metal is characterized by its ability to form such oxide, *e* = the end product was expected to be a mixture of vanadium di- and penta oxides. Formation of V_2O_5 may be due to the oxidation of vanadium dioxide in air, — = indicates that the decomposition product(s) could not be isolated and identified owing to the lack of a clear cut horizontal on the TG curve as the intermediate products are not stable to the required extent.

Table 4 TG horizontal, maxima and range of DTG and DTA peaks of bis-(5-sulphosalicylato)–diaquo complexes

Complex	Decomposition stage	Range of TG °C	Maxima of DTG trace, °C	Range of DTG effect, °C	Maxima of DTA trace, °C	Range of DTA effect, °C
(I) $Cu(5SSA)_2 \cdot 2\,H_2O$	I	100–240 ± 4	200	179–226	210 Endo.	146–226
	II	260–620 ± 2	372	353–419	380 Exo.	385–392
		433	433	433–453	480 Exo.	459–485
(II) $Ni(5SSA)_2 \cdot 2\,H_2O$	I	80–220 ± 4	172	119–185	200 Endo.	152–233
	II	230–580 ± 3	326	285–359	460 Exo.	426–492
			472	472–485	520 Exo.	506–546
(III) $Co(5SSA)_2 \cdot 2\,H_2O$	I	100–230 ± 3	200	179–219	210 Endo.	166–239
	II	250–600 ± 2	366	366–385	420 Exo.	319–433
			400	385–426	490 Exo.	485–513
(IV) $Mn(5SSA)_2 \cdot 2\,H_2O$	I	80–210 ± 3	153	133–185	190 Endo.	139–213
	II	220–570 ± 4	433	413–439	480 Exo.	466–533
(V) $Fe(5SSA)_2 \cdot 2\,H_2O$	I	90–210 ± 4	159	119–192	200 Endo.	172–226
	II	230–640 ± 3	342	300–400	470 Exo.	346–466
(VI) $VO(5SSA)_2 \cdot 2\,H_2O$	I	110–260 ± 4	219	200–246	220 Endo.	166–233
	II	353	353	319–392	490 Exo.	479–533

The TG, DTG and DTA curves reveal that these complexes decompose in a similar way to the corresponding complexes of 4-aminosalicylic acid (4ASA). Thermal decomposition starts with the loss of water, followed by pyrolysis of the dehydrated complex, resulting in metal as end-product.

As for the corresponding metal chelates of 4ASA, two decomposition periods can be distinguished in the TG curve for all six complexes of 5SSA. These two decomposition periods may be explained in accordance with the TG weight loss data, DTG and DTA results, as follows.

First decomposition period (I)

$$M(5SSA)_2 \cdot 2\,H_2O \rightarrow M(5SSA)_2 + 2\,H_2O \qquad (I)$$

In this period, two water molecules escape and an intermediate of composition $M(5SSA)_2$ is formed. This period involves a single endothermic step, as shown by the DTA curves.

Second decomposition period (II)

In this period, the dehydrated complex decomposes finally into metal oxide. This period involves one or more steps, as evident from one or more exothermic peaks in the DTA curves. The thermal decomposition of the dehydrated complex may be represented by the following possible partial reactions:

$$M(5SSA)_2 \rightarrow \begin{array}{ll} MCO_3 + \text{gaseous combustion products} & \\ \qquad H_2, CO, CO_2, H_2O & (IIa) \\ & \\ SO_2 + SO_3 + \text{sulphur} & (IIb) \end{array}$$

$$MCO_3 \rightarrow MO + CO_2 \qquad (IIc)$$

In almost all cases, the second decomposition period occurs in a longer temperature range and the partial reactions IIa, IIb and IIc usually occur in parallel, resulting in a combined step. It was difficult to separate the partial decomposition steps involved in the second decomposition period and to establish the existence of intermediates. However, in some cases the DTG curves of the complexes resolve the close-lying steps and indicate the multistep nature of the second decomposition period.

In some cases the expansion of the second decomposition period may cause error through the overlapping of two decomposition steps following one another closely. This may even give rise to the formation of a single decomposition step in the TG curve.

Shapes of DTA curves

The recorded DTA curves (Figs 1–3) are observed to have unusual shapes; however, we have compared them with those reported by earlier workers [30–32] for other salicylates, and observed that they too obtained exothermic DTA peaks with unusual shapes. Such abnormal shapes are also found for malato-aquo [33] and EDTA [34] complexes with transition metals.

The abnormal shape of the exothermic peaks in the DTA curves is probably due to the various gaseous combustion products escaping as a consequence of the decomposition of the organic skeleton, i.e. the 5-sulphosalicylate moiety of the complex. Large, broad exothermic peaks in a wide temperature range in the DTA curve for decomposition of the dehydrated complexes indicate oxidation and combustion processes besides decomposition.

Characteristic features of thermal decomposition of 5SSA complexes

(1) $Cu(5SSA)_2 \cdot 2\,H_2O$

The complex is stable up to 100°. Water molecules begin to come off in the temperature range 100–240°. Subsequently, the dehydrated complex undergoes final decomposition to CuO. The TG curve shows two horizontal sections, corresponding to the compositions $Cu(5SSA)_2$ and CuO. The DTA curve indicates one endothermic peak (210°) and two exothermic peaks (380 and 480°) (Fig. 1). The two exothermic peaks clearly indicate that the second decomposition period may take place in two distinct steps. This is supported by the corresponding DTG peaks (Fig. 1).

(2) $Ni(5SSA)_2 \cdot 2\,H_2O$

In the first decomposition period (80–210°), two water molecules escape and an intermediate of composition $Ni(5SSA)_2$ is formed. This period is characterized by an endothermic effect (Fig. 1). In the second period of decomposition (230–580°), the dehydrated complex decomposes further in two steps and finally yields a residue of NiO. The second period of decomposition is exothermic in nature, as shown by two exothermic peaks in the DTA curve. The end-product was NiO, in nearly stoichiometric amount.

(3) $Co(5SSA)_2 \cdot 2\,H_2O$

The water molecules begin to come off in the temperature range 100–230°, and the first horizontal section in the TG curve corresponds to the composition $Co(5SSA)_2$. The dehydrated complex decomposes in the range 250–600°, giving a final residue of CoO. The DTA curve shows one endothermic peak (210°), followed by two successive exothermic peaks (420 and 490°), indicating that the second decomposition period involves two steps. This is supported by the relevant section of the DTG curve (Fig. 2).

(4) $Mn(5SSA)_2 \cdot 2\,H_2O$

The thermal decomposition of this complex takes place in the temperature range 80–580°. The first decomposition period involves dehydration (80–210°), while in the second period the dehydrated complex decomposes to give a mixture of oxides. The final product was expected to be a mixture of MnO and Mn_3O_4 (Table 3). The DTA curve (Fig. 2) shows that the complex undergoes an endothermic change followed by an exothermic change on heating to 600°. The TG curve indicates a sharp inflection for dehydration and another for pyrolysis of the dehydrated complex.

(5) $Fe(5SSA)_2 \cdot 2\,H_2O$

The complex loses water in the temperature range 90–210°. The dehydrated complex breaks down above 230° and a stable residue of metal oxide is formed at about 650°. The DTA curve (Fig. 3) exhibits one endothermic peak (200°) and one large exothermic peak (470°), while the TG curve indicates two inflections for two decomposition periods. The end-product was expected to be the mixture of FeO and Fe_3O_4 (Table 3).

(6) $VO(5SSA)_2 \cdot 2\,H_2O$

Dehydration takes place in the temperature range 110–260°. Continuous decomposition is observed after dehydration; the dehydrated complex decomposes to metal oxide. The first endothermic peak (220°) in the DTA curve is due to the loss of two water molecules from the complex; this is confirmed by the TG curve, where the first inflection corresponds to the composition $(VO(5SSA)_2$ (Table 3). Pyrolysis of the dehydrated complex is an exothermal change, as shown by a large exothermic peak (490°) in the DTA curve (Fig. 3). The end-product was expected to be a mixture of vanadium di- and pentoxides.

In general, the dehydration temperature, coordinated water frequency and % metal content of the 5SSA complexes increase in roughly the same sequence as found for the SA and 4ASA complexes.

In all cases the TG weight loss data (Tables 3 and 4) demonstrated the water content and also the composition of the final residue. These results are in fair agreement with the given stoichiometry and structure of the 5SSA complexes.

Isolation of intermediates

In order to isolate intermediate dehydrated products of the thermal decomposition, samples were heated in air to an appropriate temperature in a crucible and the residues were analyzed. The decomposition products were confirmed by analytical, IR and X-ray K-absorption edge studies. However, not all intermediates of the decomposition steps could be isolated and identified, owing to the lack of a clear-cut horizontal section in the TG curve, as the intermediates are not sufficiently stable.

It is worthy of note that dehydration is accompanied by an increase in colour intensity, with a change in stereochemistry.

The IR spectra confirm the dehydration (step I), since peaks and bands characteristic of coordinated water are not present in the IR spectrum of the first decomposition product.

We earlier studied the X-ray K-absorption spectra of the Cu(II), Ni(II) and Co(II) complexes ($ML_2 \cdot 2\,H_2O$) and their dehydrated products [35], and found a change in stereochemistry from octahedral to tetrahedral as a consequence of dehydration. Details of the study will be published elsewhere.

Thermal stability

If the initial decomposition temperature measured under fixed experimental conditions is taken as a measure of the thermal stability of a complex, we can conclude that the stability of the metal complexes increases roughly in the sequence

$$\mathrm{Mn(II)} < \mathrm{Fe(II)} < \mathrm{Ni(II)} < \mathrm{Co(II)} < \mathrm{Cu(II)} < \mathrm{VO\ (II)}$$

which is in accordance with the covalency of the M—O bond.

It is interesting that the dehydration temperatures of the complexes increase with increase of the coordinated water frequency. This again follows the above sequence.

This finding may also be explained in terms of the metal contents (*M*%) of the complexes (Table 4).

Conclusions

The results of this study on the thermal decomposition of 5SSA complexes showed that thermal analysis can be useful for determination of the number of molecules of water bound, for detecting contamination in starting reagents and for control of the declared composition of a compound. It also provides a means for correlating microbial activity with the change in stereochemistry of the active species.

A knowledge of the heating curves is useful for the gravimetric analysis of a compound. For quantitative analyses, only the horizontal sections formed in the first and the last stage of decomposition are suitable; particularly the latter is of great quantitative importance.

When the heating rates were increased, the DTA and DTG peaks and the horizontal sections in the TG traces changed in the manner reported by Schultze [36].

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Zusammenfassung — Die Reaktionen des 5-Sulphosalicylat-Anions mit VO(II), Cu(II), Ni(II), Co(II), Fe(II) und Mn(II) ergaben Bis-(5-sulphosalicylato)–diaquo-Komplexe. Die Strukturen dieser Komplexe wurden durch Elementaranalyse und IR-Spektren bestätigt. Die Zersetzung der Komplexe wurde mittels TG, DTG und DTA untersucht. Die Zersetzung verläuft in zwei Schritten: Eliminierung der zwei Wassermoleküle, gefolgt von der das Metalloxid als Endprodukt ergebenden

Zersetzung des dehydratisierten Komplexes. Die Thermische Stabilität der Komplexe nimmt in der Reihenfolge VO(II) > Cu(II) > Co(II) ≈ Ni(II) ≈ Fe(II) > Mn(II) ab, womit die gleiche Reihenfolge wie für die Kovalenz der M—O-Bindung festgestellt wurde.

Резюме — Реакции 5-сульфосалицилат-иона с двухвалентными ванадил, медь, никель, кобальт, железо и марганец приводили к образованию бис-(5-сульфосалицилато)-диакво комплексов. На основе элементного анализа и ИК спектров установлена структура комплексов. Разложение комплексов было изучено методами ТГ, ДТГ и ДТА: оно протекает в две стадии: выделение двух молекул воды и последующее разложение безводного комплекса с образованием окиси металла в качестве конечного продукта. Термическая устойчивость комплексов располагается в ряд VO > Cu > Co ≈ Ni ≈ Fe > Mn, что согласуется с последовательностью ковалентности связи M—O.