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Thermal Deamination of Some Complexes of the Type $[CO(Diox \cdot H)_2(Amine)_2]X$

On the α-Dioximine Complexes of Transition Metals, LXIV.

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The thermal deamination of $[Co(diox \cdot H)_2(amine)_2]X$ type complexes were studied in dynamic temperature conditions ($diox \cdot H_2$ stands for 1,2-cycloheptanedione dioxime (heptoxime, $heptox \cdot H_2$) and 1,2-cyclo-octanedione dioxime (octoxime, $octox \cdot H_2$), amine for aniline and pyridine, X for Br, I and NCS). Kinetic parameters n, E and $\log Z$ have been derived for some derivatives by means of two computerized integral methods. The influence of the sample weight, heating rate and chemical constitution upon the kinetic parameters, as well as the kinetic compensation effect are discussed.

[Keywords: Co(III) *complexes with alycylic dioximes; Dioximine complexes of* Co(III)*; Kinetic compensation effect; Kinetics of thermal decomposition; Thermal decomposition of complexes]*

Thermische Desaminierung einiger Komplexe des Typs $[Co(Diox \cdot H)_2(Amin)_2]X$.
Über α-Dioximinkomplexe der Übergangsmetalle, LXIV.

Die thermische Desaminierung einiger Komplexe des Typs $[Co(Diox \cdot H)_2(Amin)_2]X$ wurde bei dynamischen Temperaturbedingungen untersucht [$Diox \cdot H_2$ bedeutet 1,2-Cycloheptandiondioxim, (Heptoxim, $Heptox \cdot H_2$) und 1,2-Cyclooctandiondioxim (Octoxim, $Octox \cdot H_2$), Amin bedeutet Anilin und Pyridin, X bedeutet Br, I, bzw. NCS]. Die kinetische Parameter n, E und $\log Z$ wurden mit Hilfe von zwei computergeeigneten Integralmethoden bestimmt. Der Einfluß des Gewichtes der Proben, der Heizungsgeschwindigkeit und der chemischen Zusammensetzung auf die kinetischen Parameter, bzw. der kinetische Kompensationseffekt werden diskutiert.

Introduction

The thermal decomposition of $[Co(diox \cdot H)_2(amine)_2]X$ type complexes ($diox \cdot H_2$ stands for an α-dion-dioxime, X for the external sphere anion) has been studied under dynamic temperature conditions in our earlier papers[1–3].

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If the amine is an aromatic amine or a pyridine base and X a halogen or pseudohalogen anion, the first weight loss stop on the thermogravimetric (TG) curve corresponds frequently to the loss of an amine molecule, i. e. to the substitution of this amine by the external sphere anion and to the formation of a non-electrolytic type complex:

$$[\mathrm{Co(diox \cdot H)_2(amine)_2}]X \rightarrow [\mathrm{Co(diox \cdot H)_2(amine)}X] + \mathrm{amine}$$

For these deamination reactions the apparent kinetic parameters n, E and Z, which will be referred to as reaction order, activation energy and pre-exponential factor, respectively, have been derived and the dependence of these parameters both on working conditions (sample weight m_0, heating rate q) and on chemical composition (nature of diox·H_2, amine and X) has been observed.

In the present paper the influence of sample weight and of heating rate has been studied in the case of the following complex salts:

$[\mathrm{Co(octox \cdot H)_2(pyridine)_2}]\mathrm{Br}$ (**1**), $[\mathrm{Co(octox \cdot H)_2(pyridine)_2}]\mathrm{I}$ (**2**),
$[\mathrm{Co(octox \cdot H)_2(aniline)_2}]\mathrm{NCS}$ (**3**), $[\mathrm{Co(heptox \cdot H)_2(pyridine)_2}]\mathrm{I}$ (**4**)

where octox·H_2 stands for 1,2-cyclo-octanedione dioxime (octoxime) and heptox·H_2 for 1,2-cycloheptanedione dioxime (heptoxime).

Synthesis of these complexes as well as the characterization of some new binary salts of the corresponding cations are given in the experimental part.

The second aim of this paper is to test and to compare two computerized integral methods, proposed in our previous paper[4].

Results and Discussion

Kinetic Parameters

In our TG measurements the actual weight values m_i have been determined at equal time intervals, by performing a constant heating rate. Some representative TG curves of compounds **1**—**4** are given in Fig. 1.

As seen from these TG curves, the first stage of the thermolysis is clearly the above mentioned substitution reaction with complexes **1**, **2** and **4** (curves a, b and d), i. e. a well defined plateau appears at the weight values corresponding to the loss of one molecule of pyridine and to the formation of the nonelectrolytic intermediate product.

The thermal decomposition of **3** (curve c) presents completely different features. No well defined intermediate is formed, the TG curve presents an inflexion point corresponding to the loss of about 0.5 mol of aniline. Since this inflexion appears in all cases about at the same conversion (or transformation degree) $\alpha \approx 0.5$, we have tried to derive kinetic parameters also for this not perfectly clear decomposition stage.

Some other complexes of the same type have been investigated, too. Their representative TG curves are presented in Fig. 2 and 3. As seen from these curves a well defined plateau can be observed only after the loss of the crystallization water, but the further portions of the TG curves are not consistent with the above mentioned substitution reaction, i. e. there is no evidence for the formation of a relatively stable intermediate. The TG curves of these complexes cannot be used for kinetic analysis purposes.

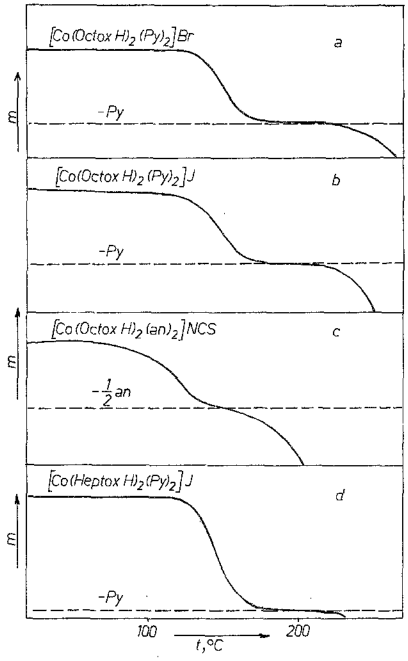

Fig. 1. Typical TG curves of the compounds 1-4 (Py stands for pyridine, an for aniline); *a* $m_0 = 100$ mg, $q = 5$ K/min; *b* $m_0 = 25$ mg, $q = 10$ K/min; *c* $m_0 = 75$ mg, $q = 10$ K/min; *d* $m_0 = 75$ mg, $q = 15$ K/min

As far as the calculation methods[4] are concerned, they have been already tested in our previous paper[1] and it has been shown, that method 1, based on the calculation of the exponential integral by using our approximation formula and performing the double minimization of a relative standard deviation, gives practically the same numerical values as method 2. Since method 1 needs about a tenfold computer time as compared to method 2, the former has been abandonned and in the present paper only methods 2 and 3 will be used.

Both of them use a *Coats—Redfern* linearization, perform the systematic variation of the n parameter in order to find the n value ensuring the maximum value for the *Jaffé* correlation coefficient ρ and calculates E from the slope of the straight line obtained[4].

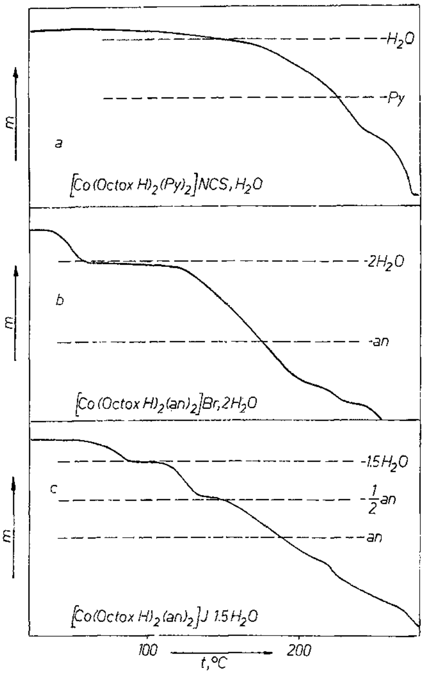

Fig. 2. TG curves of some octoxime complexes (Py stands for pyridine, an for aniline); *a* $m_0 = 100$ mg, $q = 10$ K/min; *b* $m_0 = 50$ mg, $q = 5$ K/min; *c* $m_0 = 50$ mg, $q = 5$ K/min

These methods differ from each-other only with respect to the input data.

Method 2 needs introducing of the heating rate q, of the initial and final sample weights (m_0 and m_1) corresponding to the thermal decomposition stage, as well as of the experimental sample weight (m_i) and temperature pairs (t_i °C).

Method 3 implies the graphical plot of the experimental points m_i vs. temperature, tracing of the most probable TG curve and the graphical determination of nine $\vartheta_\alpha = 10^3/T_\alpha$ values (T_α stands for the absolute temperature corresponding to the conversion α), viz. corresponding to $\alpha = 0.1, 0.2, 0.3, \ldots, 0.9$. The input data are these nine ϑ_α values and the heating rate.

Our earlier results[1] suggest method 3 to have some advantages, giving more unitary picture of the influence of working conditions upon the kinetic parameters. One might presume this superiority to be due to the partial elimination of accidental errors by tracing the most probable TG curve on the basis of the experimental points and to the more uniform repartition of the points considered (by recording m_i values at equal time intervals, one has ever more points at the beginning of the decomposition stage and less for the high slope portion of the TG curve).

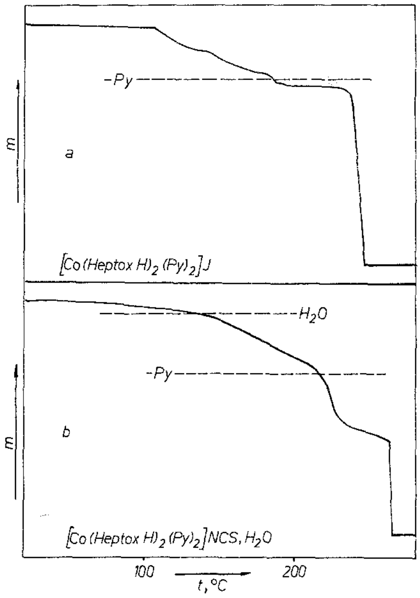

Fig. 3. TG curves of some heptoxime complexes (Py stands for pyridine): a $m_0 = 100$ mg, $q = 10$ K/min; b $m_0 = 100$ mg, $q = 5$ K/min

In the case of each complex studied 12 TG curves have been recorded by using 25, 50, 75 and 100 mg samples and heating rates of $q = 5$, 10 and 15 K/min, respectively.

By deriving kinetic parameters, very high correlation coefficient values have been obtained ($\rho > 0.99$) in all cases. This means that the

Table 1. *Kinetic parameters of the thermal deamination of some complexes of the type* [Co(*diox* · H)$_2$(*amine*)$_2$]*X by means of methods 2 and 3*

q	m_0	n		E [kJ/mol]		log Z		n		E [kJ/mol]		log Z	
K/min	mg	2	3	2	3	2	3	2	3	2	3	2	3
		[Co(octox · H)$_2$(Py)$_2$]Br (**1**)						[Co(octox · H)$_2$(Py)$_2$]I (**2**)					
5	25	2.47	2.36	253	245	30.1	28.8	1.36	1.62	181	193	20.6	22.7
	50	2.11	2.09	228	226	26.5	26.0	1.37	1.30	171	177	19.6	20.4
	75	1.62	1.67	194	201	21.9	23.2	1.33	1.40	161	169	18.1	19.2
	100	1.66	1.70	192	198	21.7	23.1	1.06	1.09	129	128	14.2	14.3
10	25	2.00	2.04	237	245	27.9	29.6	1.20	1.27	134	138	14.6	15.4
	50	2.00	2.05	221	225	25.4	26.1	0.91	0.97	119	127	12.6	13.9
	75	2.02	1.89	206	190	23.6	21.8	0.94	1.02	120	118	12.7	12.6
	100	1.84	1.92	183	185	20.6	21.1	0.77	0.75	92	88	9.4	8.9
15	25	2.72	2.83	237	231	28.7	27.5	1.34	0.88	103	101	11.1	10.5
	50	2.69	2.50	187	203	21.8	23.7	1.03	0.97	97	95	10.0	9.7
	75	1.58	1.66	136	152	15.2	16.8	0.95	1.12	93	88	9.5	9.2
	100	1.36	1.72	128	145	13.7	16.5	0.36	0.69	79	86	7.7	8.7
		[Co(octox · H)$_2$(aniline)$_2$]NCS (**3**)						[Co(heptox · H)$_2$(Py)$_2$]I (**4**)					
5	25	1.19	1.11	112	108	12.8	12.3	3.17	2.91	512	481	64.7	61.2
	50	0.64	0.91	92	104	10.1	12.2	1.39	1.59	326	311	39.8	37.9
	75	1.07	1.21	127	143	15.2	17.5	1.20	1.53	264	254	31.5	30.4
	100	0.87	0.72	101	94	12.4	10.4	1.28	1.47	251	249	29.8	29.7
10	25	1.00	1.12	104	106	11.7	12.0	2.78	3.00	341	374	42.8	46.9
	50	1.30	1.42	121	125	14.1	14.8	2.28	2.12	266	258	33.0	31.9
	75	1.17	1.30	122	130	14.5	15.4	1.36	1.45	221	243	25.6	29.0
	100	0.93	0.81	86	79	9.4	8.4	1.53	1.75	220	239	25.5	28.2
15	25	3.13	2.80	227	205	29.2	26.1	3.06	3.09	282	291	35.5	36.4
	50	1.43	1.62	124	133	15.4	16.7	2.58	2.14	258	230	31.7	27.6
	75	1.65	1.82	147	161	18.0	19.9	1.69	1.67	183	171	19.9	19.4
	100	1.71	1.46	159	127	19.6	15.0	1.67	1.80	163	169	18.7	18.8

individual TG curves can be excellently characterized by means of the kinetic parameters n, E and Z.

Results are presented in Table 1. (Z is calculated in s^{-1}).

It is obvious, that the kinetic parameters derived by both methods do not differ essentially, but they are not identical.

Influence of Working Conditions

Data presented in Table 1 show a decreasing tendency of both E and log Z with increasing sample weight as well as with increasing heating rate. This effect is very clearly expressed with compounds **1**, **2** and **4** (method 2 gives only three, method 3 a single exception, i.e. inversion of the above mentioned order).

In the case of the complex **3** no systematic variation of the kinetic parameters can be observed. This is not surprising taking into account that the shape of the TG curves is not in agreement with the substitution reaction observed with the other complexes. One can conclude that although the inflexion point of the TG curve appears about at the same conversion value, this does not indicate the formation of a well defined intermediate of the corresponding composition.

Regarding the apparent reaction orders, the values are rather scattered and no conclusion can be drawn at first view.

In order to obtain a clearer picture of the influence of working conditions upon the kinetic parameters and to have the possibility to compare the efficiency of method 3 with that of method 2, a statistical analysis of the data obtained has been performed. For this purpose mean values of the kinetic parameters have been calculated, separately for each sample weight and separately for each heating rate. Results are presented in Table 2.

One can see that in the case of compound **3** the mean values are as scattered as the individual ones, which is consistent with our above given conclusion.

The mean E and log Z values of the deamination of **1**, **2** and **4** decrease rigorously both with increasing sample weight and heating rate. The results given by methods 2 and 3 do not differ essentially, although generally the variation seems to be more uniform in the case of method 3.

A similar effect of decreasing activation energy with increasing heating rate has been observed by other authors as well[5–9]. Decreasing activation energy with increasing heating rate and with increasing sample weight have been reported in our previous papers concerning the thermal decomposition of similar and of other type complexes[10, 11].

Table 2. *Mean values of the kinetic parameters obtained for the same sample weight and heating rate values by means of methods 2 and 3*

Working conditions	n		E[kJ/mol]		$\log Z$		n		E[kJ/mol]		$\log Z$	
	2	3	2	3	2	3	2	3	2	3	2	3
	[Co(octox · H)$_2$(Py)$_2$]Br (**1**)						[Co(octox · H)$_2$(Py)$_2$]I (**2**)					
$m_0 = 25$ mg	2.40	2.41	242	240	28.9	28.6	1.30	1.23	139	144	15.4	16.2
$m_0 = 50$ mg	2.27	2.21	212	218	24.6	25.3	1.10	1.08	129	133	14.1	14.6
$m_0 = 75$ mg	1.74	1.74	179	181	20.2	20.6	1.07	1.18	125	125	13.4	13.6
$m_0 = 100$ mg	1.62	1.78	168	176	18.7	20.2	0.73	0.84	100	101	10.4	10.6
$q = 5$ K/min	1.96	1.95	217	217	25.0	25.3	1.28	1.35	160	167	18.1	19.1
$q = 10$ K/min	1.96	1.97	212	211	24.4	24.6	0.95	1.00	116	118	12.3	12.7
$q = 15$ K/min	1.84	2.18	147	183	19.8	21.1	0.92	0.89	93	92	9.6	9.5
	[Co(octox · H)$_2$(aniline)$_2$](NCS) (**3**)						[Co(heptox · H)$_2$(Py)$_2$]I (**4**)					
$m_0 = 25$ mg	1.77	1.68	148	140	17.9	16.8	3.00	3.00	378	382	47.7	48.2
$m_0 = 50$ mg	1.13	1.32	112	121	13.2	14.6	2.08	1.95	283	266	34.8	32.5
$m_0 = 75$ mg	1.30	1.44	132	145	15.9	17.6	1.44	1.55	223	223	25.7	26.3
$m_0 = 100$ mg	1.17	1.11	115	100	13.8	11.3	1.47	1.67	211	219	24.7	25.6
$q = 5$ K/min	0.94	0.99	108	112	12.6	13.1	1.76	1.85	338	324	41.4	39.8
$q = 10$ K/min	1.10	1.16	108	110	12.4	12.6	1.99	2.08	262	278	31.7	34.0
$q = 15$ K/min	1.98	1.67	164	156	20.5	19.4	2.25	2.18	221	215	26.4	25.5

The explanation of this effect, meaning that with increasing sample weight and heating rate the temperature interval corresponding to the thermal decomposition becomes larger, could be simply the limitation of the heat transfer and/or of the diffusion rate of the gaseous products evolved.

The influence of the working conditions upon the apparent reaction order n is not quite clear. It shows a decreasing tendency with increasing sample weight with compounds **1**, **2** and **4**, exactly as observed earlier in the case of analogous complexes[1]. But the influence of the heating rate is rather obscure. The n value decreases systematically with increasing q in the case of **2**, but it increases clearly in the case of **4**. In the case of complex **1** method 2 indicates a not clearly defined decreasing tendency, but method 3 shows a systematic increase of n with increasing heating rate. It is worth mentioning that in our earlier paper[10] also an increasing tendency of n with increasing q has been observed.

At any rate, by taking into account the correlation between the shape of theoretical TG curves and the value of the kinetic parameters[12] both increasing and decreasing of n with increasing heating rate could be easily understood. If the thermal decomposition rate is limited by an effect which becomes more important at higher heating rates (as heat transfer, diffusion of the gaseous product towards the air phase) the shape of the TG curves will be changed. The curve becomes flatter at higher q values, the temperature interval of the decomposition stage becomes larger), which in terms of kinetic parameters means a lower activation energy E. If this effect becomes important in an earlier stage of the decomposition step (at $\alpha < 0.5$), the shape parameter ∇ defined by us[13] as

$$\nabla = \frac{\vartheta_{0.5} - \vartheta_{0.9}}{\vartheta_{0.1} - \vartheta_{0.9}}$$

might decrease, which in terms of kinetic parameters means decreasing of the n value. If this effect becomes important only later (at $\alpha > 0.5$) the ∇ parameter increases as well as the apparent reaction order n.

General Mean Values of the Kinetic Parameters and the Kinetic Compensation Effect

Since each of the above mentioned thermal decomposition reactions has been studied under exactly the same (12) working conditions, it seems to be legitime to compare the general mean values of the kinetic parameters. These general mean values, calculated from all kinetic parameter values presented in Table 1, obtained for all working conditions used and by means of methods 2 and 3, are given in Table 3.

From the mean values of the reaction order no conclusions can be drawn.

The mean activation energy values show clear individual characteristics and seem to have some real physical meaning correlated with chemical structure. The much higher E value obtained for **1** as compared to **2** expresses the influence of the external sphere anion. This difference must be due to a different polarization effect in the case of the two anions. A similar effect has been observed in the case of some ethylenediamino-cobalt **3** complexes having also Br and I as external sphere anion[11, 14].

The great difference between the E values obtained for **2** and **4** is rather surprising, since these complexes differ only with respect to the ring size of the dioxime molecule, and for the analogous $[Co(nyox \cdot H)_2(pyridine)_2]I$ complexes ($nyox \cdot H_2$ stands for 1,2-cyclohexane dione dioxime, nyoxime) in identical working conditions a mean activation energy of $E = 111\,kJ/mol$ has been obtained[1], which is rather close to the value obtained for **2**.

Since from the kinetic parameters given in Table 1 the decomposition temperatures do not result directly, the mean value of the position parameter τ of the TG curves defined in our previous paper[13] as $\tau = \vartheta_{0.1}$ is also given in Table 3 ($10^3/\tau$ can be taken for a sort of standard decomposition temperature). Obviously, the decomposition temperature cannot be directly correlated to the activation energy, but in the case of analogous reactions of compounds having very close chemical composition, a parallelism can be observed, viz. the higher the activation energy, the higher the decomposition temperature[1]. As seen from Table 3, this effect appears clearly in the case of compounds **1** and **2**. The anomalous behaviour of **4** is obvious also in this respect. Although its activation energy is more than twice larger as compared to the E value of **2** , the decomposition temperatures of both complexes are very close to each other.

The mean values of $\log Z$ as well as its individual ones (Table 1) vary in parallel. Generally, for a given reaction these magnitudes are correlated by a

$$\log Z = aE + b$$

type kinetic compensation law, as reported in our earlier papers, too[2, 11, 15, 16]. We presumed the compensation parameter a to be even more directly correlated to the strength of the chemical bond to be broken, than the activation energy[17]. *Garn*[18] presumes this parameter to depend on a certain decomposition temperature T_c according to the relation

$$a = \frac{\log e}{R\,T_c}$$

The E and $\log Z$ values given in Table 1 excellently verify the above compensation law, as shown by the high values found for *Jaffe*'s correlation coefficient ($\rho > 0.99$) by means of the least square method.

Table 3. *General mean values of the kinetic parameters, of the position parameter* τ *and the kinetic compensation parameters*

No.	n	E[kJ/mol]	$\log Z$	τ	a' [mol/kJ]	a [mol/kJ]	b
1	1.98	202	23.4	2.457	0.128	0.129	—2.73
2	0.98	124	13.5	2.512	0.131	0.128	—2.38
3	1.30	127	15.1	2.699	0.141	0.140	—2.65
4	1.97	273	33.2	2.495	0.130	0.135	—3.71

The kinetic compensation parameters a and b are presented in Table 3, together with *Garn*'s parameter calculated as

$$a' = \frac{\tau \log e}{R} \cdot 10^{-3}$$

by using the mean τ values of Table 3 and by expressing R in kJ/(K mol), in order to have a' in K mol/kJ, as obtained a from the compensation law. As seen from Table 3, the a and a' values do not differ too much from each other, but their order is rather different. Especially the very high a value of **4** is in disagreement with the mean position parameter found. If *Garn*'s hypothesis is right, the experimentally found a parameter corresponds to a decomposition temperature of 113 °C, while the mean value of τ to 135 °C. This disagreement could be an argument against *Garn*'s hypothesis, but we believe it to be a manifestation of the already mentioned anomalous behaviour of **4**.

Experimental

Synthesis of $[Co(diox \cdot H)_2(aniline)_2]X$ *and of* $[Co(diox \cdot H)_2(pyridine)_2]X$

20 mmol of cobalt(II)acetate, 40 mmol of alycyclic dioxime (6.0 g heptoxime, 6.4 g octoxime) and 60 mmol of aniline (pyridine) were dissolved in

Table 4. *Some new complex salts of the type* $[Co(diox\cdot H)_2(amine)_2]X$; *py pyridine, an aniline*

Compound	Mol. Wt. Calcd.	Appearance	Analysis		
				Calcd.	Found
$[Co(octox\cdot H)_2(py)_2]Br$	635.5	long, brown needles	Co	9.27	9.35
		(alcohol)	Br	12.57	12.33
$[Co(octox\cdot H)_2(py)_2]NCS\cdot H_2O$	631.6	green-yellow micro-	Co	9.33	9.55
		cryst.	NCS	9.19	9.67
$[Co(octox\cdot H)_2(py)_2]I$	682.5	yellow-brown prisms	Co	8.63	8.50
		(alcohol)	I	18.60	18.45
$[Co(octox\cdot H)_2(py)_2]ClO_4$	655	yellow microcryst.	Co	8.99	9.07
$[Co(octox\cdot H)_2(an)_2]Br\cdot 2\,H_2O$	699.5	rombohedral brown	Co	8.42	8.69
		prisms (alcohol)	Br	11.42	11.79
$[Co(octox\cdot H)_2(an)_2]NCS$	641.7	green yellow crops	Co	9.18	9.11
			NCS	9.05	9.20
$[Co(octox\cdot H)_2(an)_2]1.5\,H_2O$	737.5	yellow thin prisms	Co	7.99	8.16
		(alcohol)	I	17.20	17.67
$[Co(octox\cdot H)_2(an)_2]ClO_4$	683	yellow microcryst.	Co	8.63	8.50
$[Co(heptox\cdot H)_2(py)_2]Br$	607.4	irregular long	Co	9.70	9.67
		yellow disks	Br	13.16	13.24
$[Co(heptox\cdot H)_2(py)_2]NCS\cdot H_2O$	603.6	yellow-green crops	Co	9.76	10.14
			NCS	9.62	9.86
$[Co(heptox\cdot H)_2(py)_2]I$	654.4	yellow irregular	Co	9.00	8.78
		prisms	I	19.40	19.29
$[Co(heptox\cdot H)_2(py)_2]ClO_4$	627	yellow microcryst.	Co	9.40	9.28
$[Co(heptox\cdot H)_2(an)_2]Br$	635.5	yellow prisms	Co	9.27	9.33
			Br	12.57	12.66
$[Co(heptox\cdot H)_2(an)_2]NCS$	613.6	brown-yellow micro-	Co	9.60	9.45
		cryst.	NCS	9.46	9.70
$[Co(heptox\cdot H)_2(an)_2]I$	682.5	rombohedral yellow	Co	8.63	8.55
		prisms (alcohol)	I	18.60	18.76
$[Co(heptox\cdot H)_2(an)_2]ClO_4$	655	yellow prisms	Co	8.99	8.76

Co determined complexometrically; Br, I potentiometrically with $AgNO_3$; NCS gravimetrically as $BaSO_4$; (alcohol) — recryst. from alcohol.

300 ml 75% methanol. The mixtures were oxidized by air bubbling during 3-4 h. The dark brown solutions formed were filtered. Aliquot parts of the parent solutions were treated with an excess of conc. solutions of KBr, KI, KCNS, $NaNO_3$, $NaClO_4$, respectively. The separated characteristic crystalline products were filtered off after 20-30 min standing, washed 3-4 times with water and dried on air.

Some new binary salts containing the above cations have been prepared. Their characterization is given in Table 4.

The thermal decomposition of the complexes has been investigated in the presence of air by means of a thermobalance constructed on the basis of literature data[19]. A platinum crucible has been used as sample holder.

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