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PREPARATION AND THERMAL DECOMPOSITION OF HALOGENOMETALLATES

II. Tetrachlorometallates of tris (2,2′-dipyridyl) ruthenium(II)

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Five new derivatives of general formula $[Ru(dipy)_3]MCl_4$, where M = Cu(II), Zn(II), Mn(II), Fe(II) and Co(II), and $[Ru(dipy)_3][FeCl_4]_2$ were synthesized, and their compositions and structures were confirmed by chemical analysis and electron absorptionüspectroscopy. The thermal decompositions of the compounds were studied by thermoanalytical methods. All these complexes decompose upon heating up to 1300 K, with simultaneous loss of organic fragments and structures were confirmed by chemical analysis and electron absorption spectroscopy.The exothermic effects. The residues after heating correspond to RuO_2 and the appropriate M oxides, contaminated in some cases by pure metal.

Numerous $[Ru(dipy)_3]^{2+}$ complexes (where dipy = 2,2′-dipyridyl) have been investigated intensively during the past decade, due to their interesting photochemical properties [1–5]. The reason for such widespread interest in these derivatives is the fact that they can be utilized, at least as model substances, in cyclic systems for the conversion and storage of solar energy in chemical energy. Other interesting applications of $[Ru(dipy)_3]^{2+}$ derivatives result from the possibility of their use as heterogeneous photosensitizers, e.g. in the preparation of singlet oxygen [6].

The special properties of various $[Ru(dipy)_3]^{2+}$ compounds have been intensively studied in the past (see e.g. [7] and [8] and references cited therein). However, only few efforts have been undertaken to examine the thermal behaviour of these derivatives [9, 10], including our own preliminary investigations [11, 12]. A knowledge of the thermal stabilities of $[Ru(dipy)_3]^{2+}$ complexes is essential, since this determines the possibility of their application for the above-mentioned purposes. On the other hand, these studies should help to reveal the general properties of halogenometallates of complex cations.

In this communication, the synthesis and thermal behaviour of several complexes $[Ru(dipy)_3](MCl_4)_n$ (where M = Cu(II), Zn(II), Fe(II), Mn(II), and Co(II) if $n=1$; and M = Fe(III) if $n=2$) are reported.

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Experimental

All chemicals used for syntheses were of analar grade. $[Ru(dipy)_3]Cl_2 \cdot nH_2O$ was prepared by a method described elsewhere [11, 12]. All complexes, with the exception of $[Ru(dipy)_3][FeCl_4]_2$, were synthesized by mixing stoichiometric amounts of $[Ru(dipy)_3]Cl_2 \cdot nH_2O$ and the appropriate $MCl_2 \cdot nH_2O$, both dissolved in EtOH. The resulting precipitates were separated by filtration, thoroughly washed with EtOH and dried in air at room temperature.

$[Ru(dipy)_3](FeCl_4]_2$ was prepared analogously, but water acidified with HCl was used as a medium.

Thermal analyses were carried out on an OD–103 derivatograph. The C, H, N analyses were performed on a Carlo Erba Elemental Analyzer model 1106. The amounts of Cl and M were assayed gravimetrically by standard procedures, and Ru was determined spectrophotometrically. The solid products of thermal decomposition were subjected to X-ray phase analysis using a DRON–2 diffractometer with Cu–K_α radiation. The electron absorption spectra were recorded on a Spekol–10 (Carl Zeiss, Jena) spectrophotometer.

Results and discussion

The compounds synthesized in this work have not previously been reported. In order to confirm their structures, elemental analyses were carried out, which fully proved the expected compositions (Table 1). The visible absorption spectra for all

Table 1 Elemental analyses of $[Ru(dipy)_3 [MCl_4]_n$ complexes

Compound		Found (and calculated), %					
m	*n*	C	N	H	Cl	Ru	*M*
Cu(II)	1	46.4	11.1	3.2	18.2	12.6	8.5
		(46.4)	(10.8)	(3.1)	(18.3)	(13.0)	(8.2)
Zn(II)	1	46.2	10.5	3.1	18.4	13.2	8.6
		(46.4)	(10.8)	(3.1)	(18.3)	(13.0)	(8.4)
Fe(II)	1	46.1	10.6	3.1	18.8	12.9	7.0
		(47.0)	(11.0)	(3.1)	(18.5)	(13.2)	(7.3)
Fe(III)	2	37.8	8.6	2.5	29.2	10.5	11.4
		(37.3)	(8.7)	(2.5)	(29.4)	(10.5)	(11.5)
Mn(II)	1	46.9	10.6	3.2	18.5	12.9	7.1
		(47.0)	(11.0)	(3.2)	(18.5)	(13.2)	(7.0)
Co(II)	1	46.8	10.6	3.3	18.3	13.3	7.4
		(46.8)	(10.9)	(3.1)	(18.4)	(13.1)	(7.7)

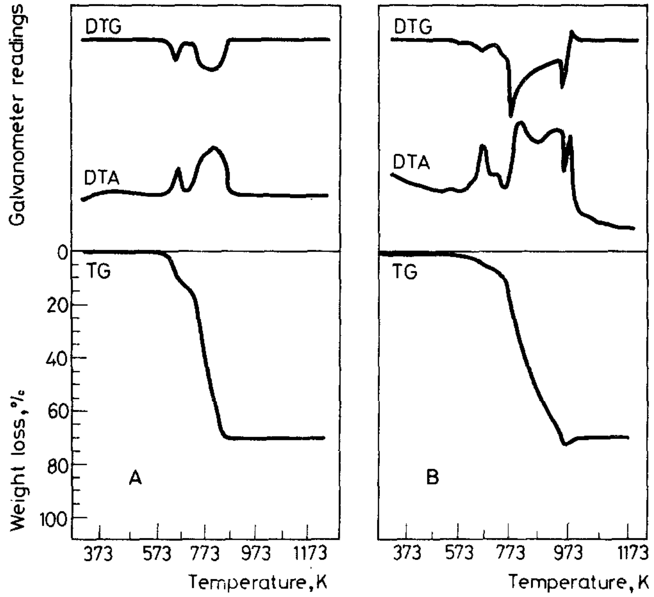

Fig. 1 Thermal analyses of [Ru(dipy)$_3$][FeCl$_4$]$_2$. *A* – mass of sample = 50 mg, *B* – mass of sample = 200 mg (for experimental details see Table 1)

compounds studied exhibit one band at ca. 450 nm. This band can be ascribed to the LMCT transition and it indicates the presence of the Ru–N bond in the molecules of these complexes [13].

An example of the results of thermoanalytical investigations in air is shown in Fig. 1. Data regarding the thermal behaviour of all the compounds are compiled in Table 2. These data reveal some general regularities. All the compounds exhibit a multistep thermal decomposition pattern. The temperatures of the onset of decomposition fall in the region 540–690 K and they depend strongly on the experimental conditions (mass of sample, heating rate, and so on). Decomposition of the compounds is accompanied by strong exothermic effects. Only in the case of the complex with Cu(II) is a weak endothermic observed at the very beginning of the thermal process. Another characteristic feature is that heating of the compounds at constant rate causes a gradual decrease in the mass of the samples, but no distinct steps can be seen in either the TG or the DTG curves. The thermogravimetric curves of some of the compounds also indicate the occurrence of processes causing an increase in the mass of samples. The residues after heating up to 1300 K correspond to RuO$_2$ and the appropriate *M* oxides (Fe$_2$O$_3$ in the case of the Fe complexes), contaminated in some cases by pure metal. These facts imply

Table 2 Thermal analyses of complexes $[Ru(dipy)_3][MCl_4]_n$

Substance		Experimental conditions^a		Temperature (K) and character^b of peaks in		Temperature, K		Total weight loss, %		
M	*n*	weight of sample, mg	heating rate, deg min^{-1}	DTA	DTG	of onset of decomposition	of completion of reaction	Assumed composition of residue^e	Theoretical	Experimental
Cu(II)	1	50	5	580w,sh (endo) (650–860 : 755) s,b (exo)	580m,sh (−) 780s,b (−)	550	860 +	$RuCl_2+CuCl_2$	60.5	73
								RuO_2+CuO	72.3	
		200	10	605w,sh (endo) (710–1070 : 780) s,b (exo)	600m,sh (−) 665w,b (−) 740s,sh (−) 1050w,sh (+)	540	1080	$Ru+Cu$	78.8	77
Zn(II)	1	200	10	(650–1010 : 725, 770, 980) s,b (exo)	(650–980:750, 880) s,b (−)	650	1030	$RuCl_2+ZnCl_2$ RuO_2+ZnO $Ru+Zn$	60.3 72.4 78.6	80
Fe(II)	1	50	5	(580–830 : 640, 730, 780) s,b (exo)	(580–810 : 600, 650, 740, 790) s,b (−)	580	840	$RuCl_2+FeCl_2$ $RuO_2+Fe_2O_3$ $Ru+Fe$	61.1 72.3 79.5	72
		100	10	(580–990 : 650, 725) s,b (exo)	(570–960 : 595, 710, 830, 925) s,b (−)	570	1000	$(RuO_2+Fe_2O_3)$		75

Fe(III)	2[d]	50	5	665m,sh (exo) 825s,b (exo)	655m,sh (−) 815s,b (−)	610	880	$RuCl_2 + FeCl_3$ $RuO_2 + Fe_3O_3$ Ru + Fe	58.6 69.7 78.0	70
		200	10	(690–1100 : 765, 805, 895, 1040, 1070) s,b (exo)	695w (−) 755w,b (−) 870s,sh (−) 1050m,sh (−) 1065w,sh (+)	690	1100			70
Mn(II)	1	100	10	(670–1160:765, 830, 870) s,b (exo)		660	1210	$RuCl_2 + MnCl_2$ $RuO_2 + MnO$ Ru + Mn (RuO_2)	61.1 73.4 79.6	73
Co(II)	1	200	10	(660–1040 : 725, 785, 990) s,b (exo)	(650–980 : 760, 900) s,b (−) 990m,sh (+)	650	1050	$RuCl_2 + CoCl_2$ ($RuO_2 + CoO$) Ru + Co	60.8 73.0 79.2	72

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[a] Other experimental conditions: all compounds studied were analysed in a ceramic crucible; α-Al_2O_3 served as a reference material; all measurements were carried out in a static atmosphere of air; sensitivities of galvanometers were 1/10, 1/10 and equal to the weight of the sample for DTA, DTG and TG, respectively.

[b] w = weak, m = medium, s = strong, sh = sharp, and b = broad; temperature ranges for unresolved peaks are indicated in parentheses (after colons, temperatures of some unresolved peaks are shown); (+) denotes an increase in weight of the sample, and (−) indicates a decrease in weight of the sample; (exo) and (endo) indicate exothermic and endothermic effects, respectively.

[c] Compounds shown in parentheses were identified by X-ray analysis of residues.

[d] See Fig. 1.

that the entire chlorine present in the compounds is released during their thermal degradation.

From this information, the following picture of the thermal degradation pathways can be outlined. The compounds start to decompose once the temperature reaches a threshold value characteristic of a given compound. Since the compounds containing MCl_4 are unstable, it is probable that the primary decomposition step is accompanied by the destruction of the original crystal structure and the formation of $[Ru(dipy)_3]Cl_2$ and MCl_2. It is characteristic however, that the thermal decomposition proceeds with the release of heat from the very beginning. This information is, of course, insufficient to allow any final conclusion. Nevertheless, it may be noted that such an effect would occur if the compounds studied were thermodynamically unstable. The temperatures of onset of decomposition of all the compounds studied in this work, as well as that of $[Ru(dipy)_3]Cl_2 \cdot nH_2O$ [11], are fairly high. This indicates that the Ru–N bond in $[Ru(dipy)_3]^{2+}$ is relatively strong. Therefore, it is not very likely that all the ligand molecules are released in unchanged form during heating. Rather, some of them are transformed to a non-volatile polymeric char, with the simultaneous release of simple volatile products. At higher temperatures, processes leading to the release of chlorine must proceed in parallel with those described above. Under the given experimental conditions, chlorine can act as a strong oxidizing agent, causing the chlorination of organic fragments. This process is predominantly responsible for the occurrence of strong exothermic effects at higher temperatures. It is worthwhile to mention that both the decomposition of $[Ru(dipy)_3]^{2+}$ and the destruction of MCl_2 or $RuCl_2$ to form chlorine and the appropriate metals can be expected to be highly endothermic processes. The decomposition in air is completed by the partial oxidation of the metals, leading to the appropriate oxides. Oxidation of the organic residue may also occur under these conditions.

The temperatures of the onset of decomposition in the series $[Ru(dipy)_3][MCl_4]$ increase in the sequence:

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

All these derivatives contain the same cation. The size of the anion may be expected to be proportional to the size of the central atom in $[MCl_4]^{2-}$. These are as follows:

$$Co^{2+} < Cu^{2+} < Fe^{2+} < Zn^{2+} < Mn^{2+}$$

According to the Kapustinskii–Yatsimirskii equation [14], the crystal lattice energy is inversely proportional to the size of the ions forming a given crystal structure. Therefore, with the above assumptions, the trend of the temperatures onset of decomposition does not correlate with the expected crystal lattice energies.

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Zusammenfassung — Fünf neue Komplexverbindungen des Typs [Ru(dipy)$_3$](MCl$_4$] (dipy = 2,2'-Dipyridyl; M = Cu, Zn, Mn, Fe, Co) sowie [Ru(dipy$_3$](FeCl$_4$]$_2$ wurden dargestellt und ihre Zusammensetzung und Struktur durch chemische Analyse und Elektronenspektroskopie bestätigt. Ihre thermische Zersetzung wurde durch simultane TG–DTA untersucht. Alle Komplexverbindungen zersetzen sich beim Erhitzen bis auf 1300 K unter gleichzeitigem Verlust der organischen Komponente und des Cl an die Gasphase. Der thermische Abbau ist von starken exothermen Effekten begleitet. Die Rückstände nach dem Erhitzen enthalten RuO$_2$ und das jeweilige Metalloxid, in einigen Fällen durch Metall verunreinigt.

Резюме — Синтезированы пять новых производных общей формулы [Ru(dipy)$_3$]MCl$_4$, где M = двухвалентные медь, цинк, марганец, железо и кобальт, а также соединение состава [Ru(dipy)$_3$][FeCl$_4$]$_2$. Состав и строение соединений был подтвержден химическим анализом и электронными спектрами поглощения, а термическое разложение комплексов было изучено термоаналитическими методами. Все комплексы разлагаются при температурах до 1300 K с одновременной потерей газообразных органических фрагментов и хлора. Термическое разложение всегда сопровождается сильными экзотермическими эффектами. Конечными продуктами разожения являлись двуокись рутения и окись соответствующего металла, содержащих в некоторых случаях чистые металлы.